

A COMPREHENSIVE TREATISE ON INORGANIC AND  
THEORETICAL CHEMISTRY

VOLUME XIV  
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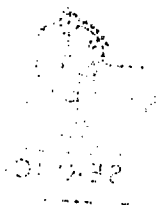
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D.Sc., F.R.S.



A COMPREHENSIVE TREATISE ON

# INORGANIC AND THEORETICAL CHEMISTRY

BY

J. W. MELLOR, D.Sc., F.R.S.

VOLUME XIV

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*WITH 277 DIAGRAMS*

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## ABBREVIATIONS

aq.	= aqueous
atm.	= atmospheric or atmosphere(s)
at. vol.	= atomic volume(s)
at. wt.	= atomic weight(s)
T° or °K	= absolute degrees of temperature
b.p.	= boiling point(s)
θ°	= centigrade degrees of temperature
coeff.	= coefficient
conc.	= concentrated or concentration
dil.	= dilute
eq.	= equivalent(s)
f.p.	= freezing point(s)
m.p.	= melting point(s)
mol(s)	= $\begin{cases} \text{gram-molecule(s)} \\ \text{gram-molecular} \end{cases}$
mol(s)	= $\begin{cases} \text{molecule(s)} \\ \text{molecular} \end{cases}$
mol. ht.	= molecular heat(s)
mol. vol.	= molecular volume(s)
mol. wt.	= molecular weight(s)
press.	= pressure(s)
sat.	= saturated
soln.	= solution(s)
sp. gr.	= specific gravity (gravities)
sp. ht.	= specific heat(s)
sp. vol.	= specific volume(s)
temp.	= temperature(s)
vap.	= vapour

In the **cross references** the first number in clarendon type is the number of the volume; the second number refers to the chapter; and the succeeding number refers to the "§," section. Thus 5. 38, 24 refers to § 24, chapter 38, volume 5.

The oxides, hydrides, halides, sulphides, sulphates, carbonates, nitrates, and phosphates are considered with the basic elements; the other compounds are taken in connection with the acidic element. The double or complex salts in connection with a given element include those associated with elements previously discussed. The carbides, silicides, titanides, phosphides, arsenides, etc., are considered in connection with carbon, silicon, titanium, etc. The intermetallic compounds of a given element include those associated with elements previously considered.

The use of **triangular diagrams** for representing the properties of three-component systems was suggested by G. G. Stokes (*Proc. Roy. Soc.*, 49. 174, 1891). The method was immediately taken up in many directions and it has proved of great value. With practice it becomes as useful for representing the properties of ternary mixtures as squared paper is for binary mixtures. The principle of triangular diagrams is based on the fact that in an equilateral triangle the sum of the perpendicular distances of any point from the three sides is a constant. Given any three substances *A*, *B*, and *C*, the composition of any possible combination of these can be represented by a point in or on the triangle. The apices of the

triangle represent the single components *A*, *B*, and *C*, the sides of the triangle represent binary mixtures of *A* and *B*, *B* and *C*, or *C* and *A*; and points within the triangle, ternary mixtures. The compositions of the mixtures can be represented in percentages, or referred to unity, 10, etc. In Fig. 1, pure *A* will be represented by a point at the apex marked *A*. If 100 be the

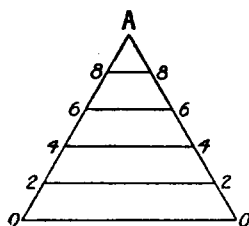


FIG. 1.

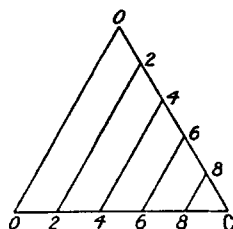


FIG. 2.

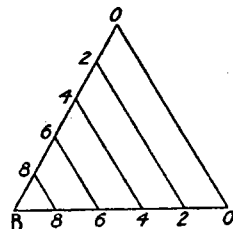


FIG. 3.

standard of reference, the point *A* represents 100 per cent. of *A* and nothing else; mixtures containing 80 per cent. of *A* are represented by a point on the line 88, 60 per cent. of *A* by a point on the line 66, etc. Similarly with *B* and *C*—Figs. 3 and 2 respectively. Combine Figs. 1, 2, and 3 into one diagram by superposition, and Fig. 4 results. Any point in this

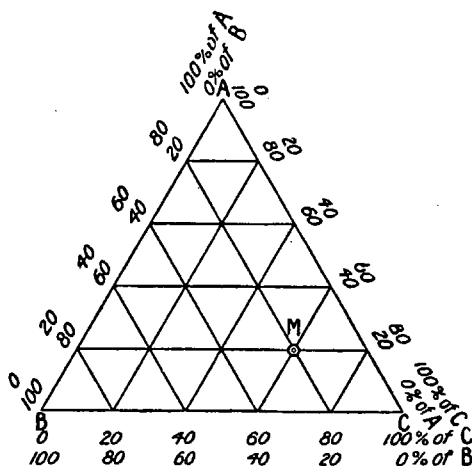


FIG. 4.—Standard Reference. Triangle.

diagram, Fig. 4, thus represents a ternary mixture. For instance, the point *M* represents a mixture containing 20 per cent. of *A*, 20 per cent. of *B*, and 60 per cent. of *C*.

## CHAPTER LXVI (*continued*)

### IRON (*continued*)

#### § 35. The Iron Fluorides

IN 1771, C. W. Scheele<sup>1</sup> dissolved iron in hydrofluoric acid but he did not obtain well-defined crystals from the soln., owing to impurities which were introduced by the action of the acid on the glass containing vessel. H. Moissan, and O. Ruff and E. Ascher observed the conditions under which fluorine attacks iron, and the iron oxides. C. Poulenc found that when iron, or anhydrous ferrous chloride is heated to redness in a current of dry hydrogen fluoride, colourless, monoclinic crystals of **ferrous fluoride**,  $\text{FeF}_2$ , are formed. The anhydrous salt was also obtained by J. J. Berzelius, and A. Scheurer-Kestner, by heating the hydrated salt out of contact with air, or better, in a current of dry hydrogen fluoride. The product obtained by A. Ferrari by heating the hydrated salt in hydrogen did not appear crystalline when examined by the X-radiogram process, but after heating the residue with ammonium fluoride in hydrogen, crystals were developed. L. Hackspill and R. Grandadam obtained it by heating iron with sodium fluoride:  $\text{Fe} + 2\text{NaF} = \text{FeF}_2 + 2\text{Na}$ ; and O. Ruff and E. Ascher, by heating ferric fluoride above  $400^\circ$ , or by reducing it with iron, ammonia, sulphur dioxide, or hydrogen.

A. Scheurer-Kestner obtained green, prismatic crystals of the *octohydrate*,  $\text{FeF}_2 \cdot 8\text{H}_2\text{O}$ , by evaporating for some days the green soln. obtained by dissolving iron in hydrofluoric acid of sp. gr. 1.07. J. L. Gay Lussac and L. J. Thénard, and J. J. Berzelius, under similar conditions, obtained the *tetrahydrate*,  $\text{FeF}_2 \cdot 4\text{H}_2\text{O}$ ; and C. Poulenc showed that the tetrahydrate is formed when the soln. containing only a little acid, is evaporated at ordinary temp. W. Biltz and E. Rahlfs observed that the addition of alcohol to the aq. soln. precipitates the tetrahydrate.

O. Ruff and E. Ascher said that the anhydrous salt is white. A. Scheurer-Kestner described the crystals of the anhydrous salt as small, yellow, quadratic prisms; and C. Poulenc, as transparent, lustrous, branching, monoclinic prisms. C. Poulenc observed that the tetrahydrate forms white, rhombohedral crystals. According to V. M. Goldschmidt, the X-radiograms show that the crystals of the anhydrous salt are tetragonal of the rutile type, like those of the anhydrous fluorides of magnesium, zinc, manganese, cobalt and nickel. The lattice dimensions are  $a = 3.83 \text{ \AA}$ ., and  $c = 3.36$ , so that  $a : c = 1 : 0.69$ ; and the distance between the iron and fluorine atoms is about  $2.11 \text{ \AA}$ . A. Ferrari gave  $a = 4.670 \text{ \AA}$ .,  $c = 3.297$ , and  $a : c = 1 : 0.706$ . C. Poulenc gave 4.09 for the sp. gr. of the anhydrous salt; and W. Biltz and E. Rahlfs, 4.09 at  $25^\circ/4^\circ$ . A. Ferrari calculated 4.333 from the lattice constants, and O. Ruff and E. Ascher, 3.95. O. Ruff and E. Ascher gave 22.9 for the mol. vol.; and V. M. Goldschmidt, and J. W. Grüner calculated values for the atomic radius of anion and cation. W. Biltz and E. Rahlfs gave 2.095 at  $20^\circ/4^\circ$  for the sp. gr. of the tetrahydrate, and 79.19 for the mol. vol.

C. Poulenc said that the anhydrous salt volatilizes at  $1100^\circ$ . K. Jellinek and A. Rudat noted that the salt is solid at  $700^\circ$ ; and W. Biltz and E. Rahlfs estimated that the m.p. exceeds  $1000^\circ$ . A. Ferrari discussed the relation between the m.p. and the space-lattice. For the dehydration of the hydrate, *vide supra*. K. Jellinek and A. Rudat gave the vap. press.,  $p$ , of the fluorine at  $773^\circ \text{ K}$ .,  $873^\circ \text{ K}$ ., and  $973^\circ \text{ K}$ .,  $p = -\log 40.05$ ,  $-\log 35.14$ , and  $-\log 31.06$  respectively; and they calculated the heat of formation to be  $(\text{Fe}, \text{F}_2) = 154.2 \text{ Cals.}$ ; O. Ruff and E. Ascher, and H. von

Wartenberg gave  $(\text{Fe}, \text{F}_2, \text{Aq.}) = 177.2$  Cals. ; E. Petersen gave  $2\text{AgF} \cdot \text{Aq.} + \text{FeCl}_2 \cdot \text{Aq.} = 2\text{AgCl} + \text{FeF}_2 \cdot \text{Aq.} + 31.8$  Cals., or  $\text{Fe}(\text{OH})_2 + 2\text{HF} \cdot \text{Aq.} = \text{FeF}_2 \cdot \text{Aq.} + 26.6$  Cals. ; and M. Berthelot gave  $(\text{Fe}, \text{F}_2, \text{Aq.}) = 127$  Cals. G. Beck discussed the free energy of the salt. R. Peters observed that ferrous fluoride in aq. soln. is probably as strongly ionized as is ferrous chloride since the electrical conductivity of a mixed soln. of ferrous chloride and sodium fluoride does not deviate much from the value calculated from the mixture rule ; and similarly also for the lowering of the f.p. of these soln.

C. Poulenc observed that at a dull red-heat, ferrous fluoride is partially reduced by *hydrogen*, and at a higher temp. the reduction is complete. K. Jellinek and A. Rudat found the equilibrium values for the reaction :  $\text{FeF}_2 + \text{H}_2 \rightleftharpoons 2\text{HF} + \text{Fe}$ ,  $\log (P_{\text{HF}}^2 / P_{\text{H}_2})$  for 500°, 600°, and 700° are respectively -2.78, -2.02, and -1.23. For the direct reduction, and the reverse reaction, with  $p$  vol. per cent. of hydrogen fluoride in the gaseous phase :

	$\text{FeF}_2 + \text{H}_2 \rightleftharpoons 2\text{HF} + \text{Fe}$			$\text{Fe} + 2\text{HF} \rightleftharpoons \text{FeF}_2 + \text{H}_2$	
$T^\circ \text{ K.}$	773°	873°	973°	773°	973°
$p$	4.0	9.3	21.5	4.7	21.3

The reduction of ferrous fluoride by hydrogen is an endothermic reaction. H. Schulze said that the anhydrous fluoride at a red-heat is not attacked by *oxygen*, but C. Poulenc observed that the anhydrous salt furnishes ferric oxide when heated in *air* or in *water* vapour. The salt dissolves slowly and sparingly in water, and the salt in aq. soln. is readily hydrolyzed with the deposition of hydrated ferric oxide. J. J. Berzelius, A. Scheurer-Kestner, and C. Poulenc observed that the hydrated salt decomposes when it is heated in air, forming ferric oxide, and this oxide is also produced when the hydrated salt is heated in hydrogen at 80°, but at a higher temp., it is reduced to iron. J. L. Gay Lussac and L. J. Thénard, J. J. Berzelius, and C. Poulenc added that the hydrated salt also dissolves sparingly in water ; and that if hydrofluoric acid be present the salt is more readily dissolved than it is in water alone.

F. Fichter and A. Goldach studied the oxidation of ferrous fluoride by *fluorine*. O. Ruff and E. Ascher found that neither *bromine* nor *iodine* has any perceptible action on ferrous fluoride. G. Gore found that anhydrous ferric fluoride is neither attacked nor dissolved by liquefied *hydrogen fluoride* ; and C. Poulenc found that in hydrogen fluoride at 1100°, crystals of ferrous fluoride are formed. The anhydrous salt and the hydrate dissolve in *hydrofluoric acid*—*vide supra*—more readily than they do in water, and the aq. soln. when treated with potassium permanganate, or exposed to air, forms ferric fluoride. A. Scheurer-Kestner observed that a soln. of ferrous fluoride in an excess of hydrofluoric acid forms ferric fluoride. When the fluoride is heated in *hydrogen chloride*, O. Ruff and E. Ascher observed that ferrous chloride is formed, but, at ordinary temp., ferrous chloride is converted into the fluoride :  $\text{FeF}_2 + 2\text{HCl} \rightleftharpoons \text{FeCl}_2 + 2\text{HF}$ . The anhydrous salt is attacked with difficulty by conc. *hydrochloric acid* ; but C. Poulenc said that the hydrated salt is readily dissolved by this acid.

O. Ruff and E. Ascher observed that anhydrous ferrous fluoride does not react with *sulphur* to any great extent ; if the product be treated with dil. hydrochloric acid, traces of hydrogen sulphide are formed. C. Poulenc observed that when heated with *hydrogen sulphide*, ferrous fluoride forms ferrous sulphide ; O. Ruff and E. Ascher, that at a red-heat, *sulphur dioxide* only deepens the colour of the salt ; and C. Poulenc, that when heated with conc. *sulphuric acid* ferric sulphate is formed. The tetrahydrate is readily soluble in sulphuric acid. O. Ruff and E. Ascher found that ferrous fluoride is slowly decomposed by *ammonia* at a dull red-heat, but, according to W. Biltz and E. Rahlfs, the tetrahydrate forms with liquid ammonia at -78.5°, or gaseous ammonia at 0°, **ferrous aquopentammino-fluoride**,  $\text{FeF}_2 \cdot 5\text{NH}_3 \cdot \text{H}_2\text{O}$ , which, at -21°, -11°, and 0°, has a heat of formation of 9.8 Cals., and the dissociation press. respectively 24, 51, and 113 mm. The sp. gr. is 1.477 at -21°, and the mol. vol. 133.4. Above 0°, this salt passes into

**ferrous aquoamminofluoride**,  $\text{FeF}_2 \cdot \text{NH}_3 \cdot \text{H}_2\text{O}$ , which at  $25^\circ$ ,  $34.5^\circ$ ,  $46.5^\circ$ , and  $61.0^\circ$ , has a heat of formation of 12.4 Cals.; and dissociation press. respectively 9.5, 18.6, 40.5, and 96.0 mm. The sp. gr. is 2.321 at  $25^\circ$ , and the mol. vol., 55.53. Above  $25^\circ$ , this salt furnishes **ferrous aquohemiamminofluoride**,  $\text{FeF}_2 \cdot \frac{1}{2} \text{NH}_3 \cdot \text{H}_2\text{O}$ . O. Ruff and E. Ascher observed that conc. *nitric acid* decomposes ferrous fluoride in the cold with the evolution of brown vapours, and the formation of a ferric salt. C. Poulenc noted that the tetrahydrate dissolves in nitric acid, forming ferric fluoride and nitrate. O. Ruff and E. Ascher found that *phosphorus*, and *arsenic* have no perceptible action on ferrous fluoride.

According to O. Ruff and E. Ascher, *carbon* has no appreciable action on ferrous fluoride. C. Poulenc observed that ferrous fluoride is insoluble in *alcohol*, and *ether*, but if water be present, the salt may be dissolved, so that the tetrahydrate dissolves in these menstrua. The salt is readily oxidized under these conditions. Ferrous fluoride is insoluble in *benzene* and it is but slightly attacked when boiled with 20 per cent. *acetic acid*. O. Ruff and E. Ascher found that when it is heated with crystalline *silicon*, ferrous fluoride is vigorously decomposed. The complex with *silicon tetrafluoride* is the so-called **ferrous fluosilicate**,  $\text{FeSiF}_6$ , (*q.v.*); that with *titanium tetrafluoride* is R. Weber's **ferrous fluotitanate**,  $\text{FeTiF}_6 \cdot 6\text{H}_2\text{O}$ ; and that with *boron trifluoride* and antipyrine is E. Wilke-Dörfurt and H. G. Mureck's **ferrous hexantipyrinoborofluoride**,  $[\text{Fe}(\text{COC}_{10}\text{H}_{12}\text{N}_2)_6](\text{BF}_4)_2$ . O. Ruff and E. Ascher found that ferrous fluoride reacts with incandescence when it is heated with *sodium*; *copper* has no perceptible action; *magnesium* reacts explosively; *zinc* reacts with a strong evolution of heat; *aluminium* reacts with a feeble detonation; *iron* has no perceptible action; a boiling 33 per cent. soln. of *sodium hydroxide* forms some sodium fluoride, but the soln. remains colourless; and fused *sodium carbonate* furnishes ferric oxide and sodium fluoride.

J. J. Berzelius, A. Scheurer-Kestner, P. Barteczko, J. C. G. de Marignac, E. Deussen, H. Kessler, and R. F. Weinland and O. Köppen reported a number of complex salts formed by ferrous fluoride. R. Wagner obtained **ammonium ferrous trifluoride**, or *ammonium trifluoferrite*,  $\text{NH}_4\text{FeF}_3 \cdot 2\text{H}_2\text{O}$ , in green octahedra, and **ammonium ferrous tetrafluoride**, or *ammonium tetrafluoferrite*,  $(\text{NH}_4)_2\text{FeF}_4$ , in brown crystals. R. Wagner could not prepare the anhydrous **potassium ferrous trifluoride**,  $\text{KFeF}_3$ , said by J. J. Berzelius to be precipitated in pale green crystals when a soln. of ferrous sulphate is added to one of potassium fluoride, instead, he obtained flesh-coloured potassium ferrous trifluoride, or *potassium trifluoferrite*,  $\text{KFeF}_3 \cdot 2\text{H}_2\text{O}$ . N. N. Ray prepared **ferrous fluoberyllate**,  $\text{FeBeF}_4 \cdot 7\text{H}_2\text{O}$ , by evaporating on the water-bath a soln. of iron and beryllium oxides in hydrofluoric acid. The salt is also obtained by the action of ferrous chloride on silver fluoberyllate, and adding alcohol to the filtered liquid. The pale green crystals of the *heptahydrate* have a sp. gr. 1.894 at  $30^\circ/4^\circ$ , and a mol. vol. of 140.95. The salt loses 4 mols. of water over conc. sulphuric acid. The **potassium ferrous tetrafluoride**, or *potassium tetrafluoferrite*,  $\text{K}_2\text{FeF}_4$ , has also been prepared. According to R. F. Weinland and O. Köppen, when hydrofluoric acid soln. of ferrous and aluminium fluorides are mixed, and concentrated over lime at ordinary temp., small greenish-white crystals of **aluminium ferrous fluoride**, or **aluminium fluoferrite**,  $\text{AlF}_3 \cdot \text{FeF}_2 \cdot 7\text{H}_2\text{O}$ , are formed.

C. W. Scheele<sup>2</sup> dissolved ferric oxide in hydrofluoric acid, but did not get a well crystallized product from the soln. because of impurities introduced by the action of the acid on the glass. H. St. C. Deville prepared **ferric fluoride**,  $\text{FeF}_3$ , by treating calcined ferric oxide with warm, conc. hydrofluoric acid, evaporating the soln. in a platinum crucible, and heating the residue until the bottom of the crucible was white-hot. There collected in the upper part of the crucible a partially-fused sublimate of colourless or greenish crystals of ferric fluoride. C. Poulenc obtained the anhydrous fluoride, in small green crystals, by passing hydrogen fluoride over red-hot iron, ferric oxide, or ferric chloride, or, by heating ammonium ferric fluoride in an inert gas—say nitrogen. O. Ruff, and O. Ruff

and E. Ascher obtained the fluoride by the action of fluorine on iron, or on ferric chloride.

A. Scheurer-Kestner, E. Deussen, and R. Peters obtained a soln. of ferric fluoride by the action of an excess of hydrofluoric acid, or of nitric acid on a soln. of ferrous fluoride in hydrofluoric acid; J. J. Berzelius, E. Deussen, G. Gallo, H. St. C. Deville, and A. W. Speransky, by dissolving ferrous hydroxide or ferric oxide in hydrofluoric acid. The evaporation of the aq. soln. furnishes flesh-coloured or colourless crystals of the hydrated fluoride. According to E. Deussen, H. Kessler, and A. Loesche, the action of hydrofluoric acid on ferric oxide is to be symbolized:  $2\text{Fe}_2\text{O}_3 + 8\text{HF} = \text{FeO} + \text{H}_2\text{O}_2 + 3\text{H}_2\text{O} + \text{FeF}_3 \cdot \text{FeF}_3 \cdot \text{FeF}_2$ , and on evaporating the soln., crystals of *ferrous fluoferriate*,  $\text{Fe}_3\text{F}_8 \cdot 10\text{H}_2\text{O}$ , are formed. A. Recoura observed that the hydrate in aq. soln. loses one-third of its fluorine when it is treated with barium chloride,  $2\text{FeF}_3 + 3\text{BaCl}_2 = \text{BaF}_2 + 2\text{BaCl}_2 + \text{Fe}_2\text{F}_4\text{Cl}_2$ ; that the trihydrate,  $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ , loses one-third of its fluorine as HF when it is heated; and that when the hydrate is boiled with alcohol two mols. of hydrogen fluoride are evolved quickly and the remainder of the fluorine very slowly. This is all taken to mean that the salt in aq. soln. is in the form of a complex  $\text{Fe}_2\text{F}_4(\text{OH})_2(\text{HF})_2 \cdot 4\text{H}_2\text{O}$ , which, at  $95^\circ$  is said to form the oxyfluoride  $\text{Fe}_2\text{F}_4\text{O}$ ; but R. Weinland and co-workers represent it by the formula  $[\text{Fe}_2\text{F}_2]\text{F}_4$ , where the  $\text{F}_4$  can be readily replaced by the radicle  $\text{SiF}_6$ . The mol. wt. of the salt in aq. soln. with 5.131, 2.879, and 1.439 per cent.  $\text{FeF}_3$  was found by A. W. Speransky to be respectively 130.1, 122.2, and 110.5; in soln. with 1.93, and 0.95 per cent.  $\text{FeF}_3$ , 118.2 and 112.7 respectively; and E. Deussen and H. Kessler, in soln. with 0.99 per cent.  $\text{FeF}_3$ , 161 to 165. R. Weinland and co-workers favoured the formula for the *hemienneahydrate*,  $\text{FeF}_3 \cdot 4.5\text{H}_2\text{O}$ , obtained by J. J. Berzelius, G. Gallo, and A. Scheurer-Kestner by evaporating the aq. soln. and drying the product over calcium chloride. When this hydrate is heated to  $100^\circ$ , A. Scheurer-Kestner, E. Deussen, A. Recoura, and R. Peters found that it passed into the *trihydrate*,  $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ .

C. Poulenc said that the crystals of the anhydrous salt are greenish, transparent, probably triclinic, and pseudorhombohedral; A. de Schulten, that they are pale green, and rhombohedral with an inclination to twinning; H. St. C. Deville, that they are isomorphous with those of aluminium fluoride; and O. Ruff and E. Ascher, that they are isomorphous with those of aluminium fluoride; and O. Ruff and E. Ascher, that they are hexagonal like cobaltic fluoride, and that the X-radiograms show a lattice with  $a=7.78 \text{ \AA}$ ,  $c=3.73 \text{ \AA}$ , and  $a:c=1:0.479$ . There are 4 mols. per unit cell. F. Ebert gave for the rhombohedral lattice  $a=3.756 \text{ \AA}$ , and  $\alpha=88^\circ 14.5'$ , and for the hexagonal lattice,  $a=5.201 \text{ \AA}$ , and  $c=6.660 \text{ \AA}$ , and  $a:c=1:1.28$ . The vol. of the rhombohedral lattice is  $52.06 \text{ \AA}^3$ , and there is one mol. per cell. The calculated sp. gr. is 3.56; and the observed value 3.52. W. Nowacki, and N. Wooster made observations on the subject. J. A. A. Ketelaar found that the crystals are isomorphous with the trifluorides of cobalt, aluminium, rhodium, and palladium. A. Scheurer-Kestner said that the crystals of the hemienneahydrate are colourless; G. Gallo, greenish; J. J. Berzelius, pale flesh-red; and R. Weinland and co-workers, pale rose-red. C. Poulenc gave 3.87 for the sp. gr. of the salt; O. Ruff and E. Ascher, 3.52, when the value calculated from the lattice constants is 3.81. A. Speransky found the lowering of the f.p. of aq. soln. with 5.131, 2.879, and 1.439 per cent. of  $\text{FeF}_3$  to be respectively  $0.745^\circ$ ,  $0.445^\circ$ , and  $0.245^\circ$ . Observations were also made by R. Peters, and H. Kessler. K. Jellinek and A. Rudat found that the salt is solid at  $550^\circ$ , and C. Poulenc, that it volatilizes above  $1000^\circ$  without melting. K. Jellinek and A. Rudat gave the vap. press.,  $p$ , of the fluorine at  $623^\circ \text{ K}$ ,  $723^\circ \text{ K}$ , and  $823^\circ \text{ K}$ .  $\log p = -49.05$ ,  $-41.91$ , and  $-35.59$  respectively. According to A. Scheurer-Kestner, if the trihydrate be heated above  $100^\circ$ , dehydration is accompanied by decomposition; E. Deussen added that even at  $100^\circ$ , a small proportion is decomposed; and G. Gallo observed that when the salt is warmed at  $150^\circ$  to  $200^\circ$ , it is completely converted into ferric oxide and

hydrogen fluoride. K. Jellinek and co-workers calculated for the heat of formation of ferric fluoride ( $\text{Fe}_2\text{F}_6$ ) = 233.25 Cals. at 800° K. The thermal value of the reaction  $\text{FeF}_2 + \frac{1}{2}\text{F}_2 = \text{FeF}_3$  is very nearly half the heat of formation of  $\text{FeF}_2$ , indicating that the three fluorine atoms are symmetrically placed in the molecule, and have each the thermal value 78.00 Cals. M. Berthelot gave  $(2\text{Fe}_2\text{F}_6, \text{Aq.}) = 335.1$  Cals.; E. Petersen gave  $2\text{FeCl}_3, \text{Aq.} + 6\text{AgF}, \text{Aq.} = 2\text{FeF}_3, \text{Aq.} + 6\text{AgCl} + 93.8$  Cals., and hence calculated 23.2 to 23.9 Cals. for  $\text{Fe}(\text{OH})_3, \text{Aq.} + 3\text{HF}, \text{Aq.}$ . O. Ruff and E. Ascher calculated from H. von Wartenberg's data,  $(\text{Fe}_2\text{F}_6, \text{Aq.}) = 243.1$  Cals. The heat of solution is  $\text{FeF}_3, \text{Aq.} + 6\text{HF}, \text{Aq.} = 1.2$  Cals.

J. J. Berzelius noted that sat. soln. of ferric fluoride are colourless; and A. Byk and H. Jaffe found that for 1 cm. layers of ferric fluoride dissolved in conc. hydrofluoric acid, the absorption spectrum,  $\lambda$ , was respectively 2727, 2700, 2584, and 2448 Å. with soln.  $\frac{1}{2}$ ,  $\frac{1}{5}$ , and  $\frac{1}{50}$ th the initial concentration. According to A. W. Speransky, the sp. electrical conductivity,  $K$ , and the conductivity,  $\mu$ , for soln. with a mol of salt in  $v$  litres, are:

$v$	6	12	24	48	96
$K$	0.001565	0.000925	0.000563	0.000359	0.000237
$v$	3.925	5.887	8.883	13.247	19.87
$\mu$	7.6	8.4	9.3	10.4	11.9

The aq. soln. is therefore a poor conductor. R. Weinland and co-workers obtained  $\mu=39$  for  $v=128$ . A. Recoura noted that the hydrolysis of aq. soln. of ferric fluoride is not so great as is the case with soln. of other ferric salts, since the soln. is colourless. This is in agreement with the comparatively small electrical conductivity, and also with A. W. Speransky's observations on the influence of soln. of ferric fluoride on the inversion of cane sugar. R. Peters said that the hydrolysis is perceptible with a dilution  $v=96$ . R. H. Carter observed that the  $\text{H}^+$ -ion conc. of a sat. soln. is  $p_{\text{H}}=3.0$ , at 25°. If the temp. be augmented, the hydrolysis is greater. J. M. Ordway, for instance, observed that half the iron is precipitated as hydrated oxide when a 0.3 per cent. soln. is boiled. P. Nicolardot also observed that the colloidal hydroxide is produced in hot aq. soln., and this colours the liquid yellow. Unlike soln. of ferric chloride, A. Scheurer-Kestner, and J. M. Ordway observed that soln. of ferric fluoride do not dissolve hydrated ferric oxide. A. Recoura, and R. Weinland and co-workers showed that the degree of ionization of soln. of ferric fluoride is small; and J. Knobloch, L. Szebelledy, and C. Bongiovanni said that ferric ions in aq. soln. of the fluoride do not appear when the soln. is tested with thiocyanate, salicylate, or acetic acid, and antipyrine, and iodine is not liberated from iodides. E. Deussen said that the reactions of  $\text{Fe}^{++}$ -ions appear after the soln. has been treated with sulphuric or acetic acid. The smaller conc. of  $\text{Fe}^{++}$ -ions in soln. of ferric fluoride than in soln. of other ferric salts was found by R. Peters to be in harmony with the observation that the reduction potential of a soln. of a ferric salt is raised by the addition of  $\text{F}^-$ -ions owing to the removal of the  $\text{Fe}^{++}$ -ions; and in accord with the fact that the conductivity and lowering of the f.p. of mixed soln. of sodium fluoride and ferric chloride are less than the values of these constants calculated by the mixture rule. N. R. Dhar and G. Urbain found that the polarization of iron in soln. of ferric fluoride, agrees with the assumption that complexes are formed in the soln.—*vide supra*. A. Heydweiller studied the dielectric constant of the hydrated salt.

E. Feytis measured the magnetic susceptibility,  $\chi$  mass units, of the trihydrate and obtained at 13°,  $\chi=47.3 \times 10^{-6}$  per gram, or  $7899 \times 10^{-6}$  per mol. P. Weiss calculated from E. Feytis' measurements the magneton number of the trihydrate to be 23. T. Ishiwara calculated the magnetic susceptibility from P. Pascal's datum for a soln. of the salt,  $\chi=45.5 \times 10^{-6}$ , and for the solid, at 16.5°, he obtained  $47.3 \times 10^{-6}$ . K. Honda and T. Ishiwara observed that the susceptibility decreases with a rise of temp., at first slowly, then rapidly, thus:

$\chi \times 10^6$	99.4°	66.8°	39.8°	12.3°	-3.3°	-27.5°	-66.5°	-105.7°	-162.1°
	42.8	44.8	46.1	47.6	48.7	50.0	52.2	54.0	55.0



According to C. Poulenc, *hydrogen*, at a dull red-heat, reduces ferric fluoride to ferrous fluoride and to the metal. K. Jellinek and A. Rudat found for equilibrium in  $2\text{FeF}_3 + \text{H}_2 \rightleftharpoons 2\text{FeF}_2 + 2\text{HF}$ ,  $\log(p^2_{\text{HF}}/p_{\text{H}_2})$  is  $-3.06$ ,  $-1.71$ , and  $-0.52$  respectively at  $350^\circ$ ,  $450^\circ$ , and  $550^\circ$ ; and for the value of  $p$  vol. per cent. of hydrogen fluoride, respectively  $2.9$ ,  $13.0$ , and  $42.0$ . The processes of reduction of ferric chloride to ferrous chloride and to iron are endothermal. C. Poulenc found that when ferric fluoride is heated in *air* it readily forms ferric oxide. E. Deussen noted that when the trihydrate is exposed to air, its colour changes from yellow to yellowish-brown, and the proportion of iron is increased; but A. Recoura found that the salt is not changed in dried air. As indicated above, A. Scheurer-Kestner observed that the hydrated salt cannot be heated above  $100^\circ$  without decomposition, and C. Poulenc found that when the salt is heated in *water vapour*, ferric oxide is formed. C. Poulenc, and A. Byk and H. Jaffe noted that the anhydrous salt is sparingly soluble in hot or cold water, and the process of dissolution is slow. A. Recoura said that a cold sat. soln. contains 8 per cent. of  $\text{FeF}_3$ ; and R. H. Carter found  $0.091$  grm.  $\text{FeF}_3$  per 100 c.c. of a sat. soln. at  $25^\circ$ . J. J. Berzelius, and A. Scheurer-Kestner also observed that the hydrated salt dissolves in water; and A. Loesche said that one part of the trihydrate dissolves in 80 parts of water. The hydrolysis of the aq. soln. has been discussed above. Well-defined basic salts—**ferric oxyfluorides**—have not been prepared. J. J. Berzelius, and A. Scheurer-Kestner reported that on adding ammonia to the aq. soln. of ferric fluoride, a reddish-brown liquid is not formed as in the case of ferric chloride, but a yellow precipitate of a basic fluoride is formed to which J. J. Berzelius assigned the formula  $3\text{Fe}_2\text{O}_3 \cdot 2\text{FeF}_3 \cdot 4\text{H}_2\text{O}$ , or  $\text{Fe}_8\text{F}_6\text{O}_9 \cdot 4\text{H}_2\text{O}$ ; A. Scheurer-Kestner,  $\text{Fe}_2\text{O}(\text{OH})_3\text{F}$ ; and P. Nicolardot,  $\text{Fe}_2\text{O}_3 \cdot \text{HF} \cdot \text{H}_2\text{O}$ . A. Loesche added that the precipitate obtained by treating the aq. soln. with ammonia has no constant composition. Other oxyfluorides have been mentioned without a demonstration that they are chemical individuals. Thus, E. Deussen reported one to be formed by the action of hydrofluoric acid on hammer-scale; A. Recoura,  $\text{Fe}_2\text{F}_4\text{O}$ , as described above; and C. Poulenc, the formation of a basic salt by hydrolysis.

O. Ruff and E. Ascher observed that *bromine* and *iodine* have no perceptible action on ferric fluoride. C. Poulenc obtained the salt in crystals by heating it in *hydrogen fluoride* at  $1000^\circ$ ; and K. Fredenhagen said that the salt is not perceptibly soluble in liquid hydrogen fluoride. O. Ruff and E. Ascher added that the evaporation of a soln. of the salt in 40 per cent. *hydrofluoric acid* yields a hydrate which is readily hydrolyzed by water. A. Byk and H. Jaffe observed that although ferric fluoride is sparingly soluble in water, it readily dissolves in hydrofluoric acid. K. Fredenhagen and G. Cadenbach studied the subject. C. Poulenc showed that when the salt is heated in a current of *hydrogen chloride*, ferric chloride is formed, and at ordinary temp. the reaction is reversed:  $\text{FeF}_3 + 3\text{HCl} \rightleftharpoons \text{FeCl}_3 + 3\text{HF}$ . Boiling or cold *hydrochloric acid* has very little action on ferric fluoride; and E. Petersen said that the action of dil. hydrochloric acid on an aq. soln. of ferric fluoride is endothermal. J. Knobloch, C. Bongiovanni, and L. Szebelledy observed that a soln. of ferric fluoride, unlike soln. of ferric salts in general, does not liberate iodine from a soln. of *potassium iodide*. O. Ruff and E. Ascher found that there is no perceptible reaction between ferric fluoride and *sulphur*, although when the product is treated with dil. hydrochloric acid, traces of hydrogen sulphide appear. C. Poulenc observed that at a red-heat *hydrogen sulphide* forms hydrogen fluoride and ferrous sulphide. O. Ruff and E. Ascher found that *sulphur dioxide* slowly reduces ferric to ferrous fluoride. According to C. Poulenc, ferric fluoride is attacked with difficulty, even by boiling *sulphuric acid*. O. Ruff and E. Ascher observed that ferric fluoride is to some extent reduced when it is heated in *ammonia*, forming ferrous and ammonium fluorides. C. Poulenc observed that ferric fluoride is only slightly attacked, even by boiling *nitric acid*. O. Ruff and E. Ascher observed no perceptible reaction when ferric fluoride is heated with red *phosphorus*, or with *arsenic*; nor is there any reaction with *carbon*. C. Poulenc said that ferric

fluoride is insoluble in *alcohol*, and *ether*; and O. Ruff and E. Ascher, that it is insoluble in ether and *benzene*. A. Scheurer-Kestner found that the hydrated fluoride is also insoluble in alcohol. O. Ruff and E. Ascher found that the fluoride is feebly attacked by boiling, 12 per cent. *acetic acid*. R. Weinland and W. Hübner studied the complexes formed with *oxalic acid*. E. Böhm showed that when heated with a soln. of *potassium acetate*, ferric fluoride is decomposed. According to J. Knobloch, L. Szebelledy, and C. Bongiovanni, as indicated above, a soln. of ferric fluoride, unlike soln. of ferric salts in general, does not give colorations with *potassium thiocyanate*, *acetic acid* and *antipyrine*, or *salicylic acid*. F. Calzolari observed that ferric fluoride probably forms a complex salt with *antipyrine*. R. Weinland and co-workers obtained complex salts with *guanidine*,  $\text{H}_2(\text{CN}_3\text{H}_5)_2[\text{FeF}_5(\text{H}_2\text{O})]$ ; with *ethylenediamine*,  $\text{H}_2\text{en}[\text{FeF}_5(\text{H}_2\text{O})]$ ; and with *pyridine*,  $\text{H}_2(\text{C}_5\text{H}_5\text{N})_2[\text{FeF}_5(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ , and  $\text{H}(\text{C}_5\text{H}_5\text{N})[\text{FeF}_4] \cdot \text{H}_2\text{O}$ . J. Nicklès noted that ferric fluoride forms complexes with *quinine*, and *brucine*. A. Recoura also obtained a complex with *silicon tetrafluoride*,  $\text{FeF}_3 \cdot \text{SiF}_4$ . H. St. C. Deville and H. Caron noted that when ferric fluoride is heated with *boric oxide*, in the absence of air, ferric oxide and boron fluoride are formed. O. Ruff and E. Ascher observed that when ferric fluoride is heated with crystalline *silicon*, the attack is attended by a glow; *sodium* also reacts with incandescence; no perceptible reaction occurs with *copper*; *magnesium* reacts explosively; *zinc* reacts with the evolution of much heat; and similarly with *aluminium*; whilst *iron* reacts strongly when heated with ferric fluoride, forming ferrous fluoride. A boiling, 33 per cent. soln. of *sodium hydroxide* acquires a colour, and brown hydrated ferric oxide is deposited. C. Poulenc noted that molten *sodium carbonate* converts the fluoride into ferric oxide and sodium fluoride. A. Recoura—*vide supra*—studied the action of *barium chloride* on the aq. soln. and it resulted in the formation of **ferric fluochloride**,  $\text{Fe}_2\text{F}_4\text{Cl}_6$ .

The complex salts were discussed by P. Barteczko, and R. Weinland and co-workers, and, according to H. von Helmolt, they form isomorphous series with the complex aluminium and chromium fluorides. R. Weinland and co-workers prepared **ammonium tetrafluoferrate**,  $\text{NH}_4[\text{FeF}_4]$ ; crystals of **ammonium hexafluoferrate**,  $(\text{NH}_4)_3[\text{FeF}_6]$ , were prepared by R. Wagner, and the salt was studied by P. Weiss and E. Feytis, L. Pauling, H. von Helmolt, and J. C. G. de Marignac. J. Nicklès found that the mixed soln. of ferric and ammonium fluorides, or that obtained by mixing ammonium fluoride with ferric chloride, furnishes **ammonium ferric fluoride**, or **ammonium pentafluoferrate**,  $(\text{NH}_4)_2\text{FeF}_5$ , but J. C. G. de Marignac showed that the salt has the composition  $(\text{NH}_4)_3\text{FeF}_6$ . The crystals are small, colourless, regular octahedra, with no birefringence. L. Pauling found that the cubic crystals of **ammonium ferric hexafluoride**,  $(\text{NH}_4)_3\text{FeF}_6$ , have a face-centred lattice, containing 4 mols., with  $a=9.10 \text{ \AA}$ . H. Seifert studied the subject. J. Nicklès found that the crystals do not lose weight in air at  $100^\circ$ , but when roasted in air, ferric oxide is formed. The salt is less soluble in water than the corresponding potassium salt, and the boiling aq. soln. is hydrolyzed, and yellow flecks of an hydroxide or basic salt separate. Lead acetate gives a precipitate which is yellow when hot; lead nitrate, a precipitate which is not yellow. Bismuth nitrate gives a white precipitate from the hot soln.; ammonia precipitates hydrated ferric oxide; potassium ferrocyanide, and gallic acid give blue precipitates; and potassium thiocyanate, a red precipitate. H. Remy and H. Busch prepared a number of substituted ammonium salts—*e.g.*, the **methylammonium ferric fluorides**:  $\{\text{NH}_3(\text{CH}_3)\}\text{FeF}_4$ ;  $\{\text{NH}_3(\text{CH}_3)_2\}\text{FeF}_5$ ; and  $\{\text{NH}_3(\text{CH}_3)_3\}\text{FeF}_6$ ; the **dimethylammonium ferric fluorides**:  $\{\text{NH}_2(\text{CH}_3)_2\}\text{FeF}_4 \cdot \text{H}_2\text{O}$ ;  $\{\text{NH}_2(\text{CH}_3)_2\}_2\text{FeF}_5 \cdot 2\text{H}_2\text{O}$ ;  $\{\text{NH}_2(\text{CH}_3)_2\}_2\text{FeF}_4 \cdot \text{HF}_2$ ; and  $\{\text{NH}_2(\text{CH}_3)_2\}_3\text{FeF}_6 \cdot 2\text{HF}$ ; the **trimethylammonium ferric fluoride**:  $\{\text{NH}(\text{CH}_3)_3\}_2\text{FeF}_5 \cdot 2\text{HF}$ ; the **tetramethylammonium ferric fluoride**:  $\{\text{N}(\text{CH}_3)_4\}\text{FeF}_4 \cdot \text{H}_2\text{O}$ ; **ethylammonium ferric fluorides**:  $\{\text{NH}_3(\text{C}_2\text{H}_5)\}_2\text{FeF}_5 \cdot \text{HF}$ ; and  $\{\text{NH}_3(\text{C}_2\text{H}_5)\}_3\text{FeF}_6 \cdot 2\text{HF}$ ; **propylammonium ferric fluorides**:  $\{\text{NH}_3(\text{C}_3\text{H}_7)\}_2\text{FeF}_5 \cdot \text{HF}$ ; and  $\{\text{NH}_3(\text{C}_3\text{H}_7)\}_3\text{FeF}_6 \cdot 2\text{HF}$ ; **butyl-**

**ammonium ferric fluorides** :  $\{\text{NH}_3(\text{C}_4\text{H}_9)\} \cdot \text{FeF}_4 \cdot 2\text{H}_2\text{O}$  ;  $\{\text{NH}_3(\text{C}_4\text{H}_9)\}_2 \cdot \text{FeF}_5 \cdot \text{HF}$  ; and  $\{\text{NH}_3(\text{C}_4\text{H}_9)\}_3 \text{FeF}_6 \cdot 2\text{HF}$ .

E. Wilke-Dörfurt and H. G. Mureck obtained *ferric hexantipyridinoborofluoride*,  $[\text{Fe}(\text{COC}_{10}\text{H}_{12}\text{N}_2)_6](\text{BF}_4)_3$ . R. F. Weinland and co-workers prepared *pyridinium tetrafluoroferrate*,  $[(\text{C}_5\text{H}_5\text{N})\text{H}][\text{FeF}_4] \cdot \text{H}_2\text{O}$  ; *pyridinium pentafluoroferrate*,  $[(\text{C}_5\text{H}_5\text{N})_2\text{H}_2][\text{FeF}_5] \cdot \text{H}_2\text{O}$  ; *ethylenediaminoammonium pentafluoroferrate*,  $[\text{en}_2\text{H}_2][\text{FeF}_5] \cdot \text{H}_2\text{O}$  ; and *guanidinium pentafluoroferrate*,  $[(\text{CH}_3\text{N}_3)_2\text{H}_2][\text{FeF}_5] \cdot \text{H}_2\text{O}$ . H. Busch obtained *methylammonium*, *dimethylammonium*, *trimethylammonium*, *tetramethylammonium*, *ethylammonium*, *propylammonium*, and *butylammonium fluoroferrates*.

J. J. Berzelius, J. Nicklès, and P. Guyot prepared **potassium hexafluoroferrate**, or *potassium ferric hexafluoride*, which they represented as  $4\text{KF} \cdot 2\text{FeF}_3 \cdot \text{H}_2\text{O}$ . A. Greeff, and P. Guyot studied this compound. R. Weinland and co-workers prepared **potassium tetrafluoroferrate**,  $\text{K}[\text{FeF}_4]$  ; and J. J. Berzelius, **potassium pentafluoroferrate**,  $\text{K}_2[\text{FeF}_5]$ . J. Nicklès obtained crystals of the hemihydrate, and O. T. Christensen, crystals of the monohydrate. R. Wagner showed that the composition is best represented by  $\text{K}_3[\text{FeF}_6]$ . The potassium salt resembles the ammonium salt. F. Röder prepared **sodium pentafluoroferrate**,  $\text{Na}_2[\text{FeF}_5]$ , and J. Nicklès, the hemihydrate. J. J. Berzelius, and J. Nicklès, prepared **sodium ferric fluoride**, or **sodium hexafluoroferrate**, in an analogous manner. The salt is also obtained as a white, crystalline precipitate by adding ferric chloride or fluoride to a neutral soln. of sodium fluoride. J. Nicklès represented the composition of the salt by the formula  $4\text{NaF} \cdot 2\text{FeF}_3 \cdot \text{H}_2\text{O}$ , but R. Wagner showed that the salt has the composition  $\text{Na}_3\text{FeF}_6$  ; and A. Greeff added that it does not give a red coloration with potassium thiocyanate, which shows that the iron atom is part of the anion. R. Peters obtained the *hemihydrate*,  $2\text{Na}_3\text{FeF}_6 \cdot \text{H}_2\text{O}$ . According to A. V. Baskoff, sodium and ferric fluorides form a eutectic mixture which melts at  $892^\circ$ , and contains 65 molar per cent. of sodium fluoride. R. Wilke observed that sodium salts precipitate from soln. of ferric fluoride the salt  $\text{Na}_3\text{FeF}_6$ , or *iron cryolite*. R. Weinland and co-workers prepared blue **copper hexafluoroferrate**,  $(\text{FeF}_6)_2[\text{Cu}(\text{H}_2\text{O})_6]$  ; and colourless **silver pentafluoroferrate**, or silver fluoroferrite,  $\text{Ag}_2[\text{FeF}_5(\text{H}_2\text{O})]_2 \cdot 2\text{H}_2\text{O}$ . A. Recoura reported **barium hexafluoroferrate**,  $\text{Ba}_3(\text{FeF}_6)_2$ , to be formed as a precipitate when a soln. of barium chloride is added to one of ferric fluoride. R. F. Weinland and O. Köppen prepared **zinc pentafluoroferrate**,  $\text{ZnFeF}_5 \cdot 7\text{H}_2\text{O}$ , by mixing soln. of the component salts. The solid is colourless in thin layers, red in thick layers. It is sparingly soluble in dil. hydrofluoric acid, and does not effloresce over conc. sulphuric acid. The corresponding **cadmium pentafluoroferrate**,  $\text{CdFeF}_5 \cdot 7\text{H}_2\text{O}$ , or  $[\text{FeF}_5(\text{H}_2\text{O})][\text{Cd}(\text{H}_2\text{O})_6]$ , was also prepared. F. Ephraim and P. Barteczko prepared **thallous ennefluoroferrate**,  $3\text{TlF} \cdot 2\text{FeF}_3$ , or  $\text{Tl}_3(\text{Fe}_2\text{F}_9)$ , in pink crystals, by evaporating a soln. of thallous fluoride and an excess of ferric fluoride. R. Weinland and co-workers also obtained the rose-red salt  $\text{Tl}_2[\text{FeF}_5(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ . R. F. Weinland and O. Köppen obtained **ferrous pentafluoroferrate**,  $\text{Fe}''\text{Fe}'''\text{F}_5 \cdot 7\text{H}_2\text{O}$ , or  $\text{FeF}_3 \cdot \text{FeF}_2 \cdot 7\text{H}_2\text{O}$ , or  $[\text{Fe}'''\text{F}_5(\text{H}_2\text{O})][\text{Fe}''(\text{H}_2\text{O})_6]$ , or  $\text{Fe}(\text{FeF}_5) \cdot 7\text{H}_2\text{O}$ , in yellow crystals by the action of ferrous carbonate on a hydrofluoric acid soln. of hydrated ferric oxide. They also prepared **cobalt pentafluoroferrate**,  $\text{Co}(\text{FeF}_5) \cdot 7\text{H}_2\text{O}$  ; and **nickel pentafluoroferrate**,  $\text{Ni}(\text{FeF}_5) \cdot 7\text{H}_2\text{O}$ , in a similar manner. *Vide supra*, for E. Deussen's  $\text{FeF}_2 \cdot 2\text{FeF}_3 \cdot 10\text{H}_2\text{O}$ .

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### § 36. The Iron Chlorides—Ferrous Chloride

Iron forms two chlorides—ferrous chloride,  $\text{FeCl}_2$ ; and ferric chloride,  $\text{FeCl}_3$ . E. Darmstädter<sup>1</sup> suggested that the vague and indefinite remarks on the sublimation of vitriol, by Geber, in his *Summa perfectionis*, might refer to sublimed ferric chloride prepared by heating ferric oxide with sal ammoniac. In 1648,

J. R. Glauber prepared iron chloride by dissolving iron in hydrochloric acid, and evaporating the soln. He thus obtained an impure chloride as a blood-red mass of ferric chloride. The crystals when placed in a soln. of potassium silicate, furnished a branched structure which was later called *Glauber's iron tree*. R. Boyle, in 1690, obtained crystals from a soln. of iron in hydrochloric acid, and found that they were soluble in spirits of wine. The alcoholic soln. of the iron chloride afterwards acquired some celebrity as a medicine under various names—e.g., *Bestuscheff's tinctura tonico-nervina*, named after the Russian General Bestuscheff; and *Lamotte's gold drops*, named after the French officer, M. Lamotte—and its mode of preparation was kept secret until about the end of the eighteenth century. M. Neumann, C. W. Juch, J. B. van Mons, G. Kerner, F. W. Krüger, and M. H. Klaproth described its preparation by heating a mixture of iron pyrites and mercuric chloride, isolating the iron salt from the products of the reaction, and dissolving the salt in rectified wine. The anhydrous sublimed chlorides were discussed by F. A. C. Gren in 1795; and H. Davy, and J. Davy showed the relation between the composition and nature of the two chlorides.

The presence of ferrous chloride has been observed in native iron—e.g., that of Ovivak, Greenland—and in meteorites—e.g., that of Claiborne, Alabama, etc.—by C. T. Jackson,<sup>2</sup> J. L. Smith, etc. The chloride is often accompanied by some nickel chloride,  $\text{NiCl}_2$ . The ferrous chloride is coloured green to brown. The ferrous chloride occurring under these conditions was called **lawrencite**, by A. Daubrée—after J. Lawrence Smith. In some cases, ferric chloride formed by the oxidation of lawrencite exudes from the surface of meteoric iron in drops, called by A. Daubrée, *stigmatite*—from *στάγμα*, drops. The existence of ferrous chloride in the sublimates at Vesuvius was demonstrated by T. Monticelli and N. Covelli. J. T. Conroy observed its formation in the superheater of the decomposer of a chlorine plant.

**The formation and preparation of ferrous chloride.**—Anhydrous ferrous chloride can be obtained by the action of chlorine on heated iron (*q.v.*), as recommended by L. J. Thénard,<sup>3</sup> but it is difficult to prevent the chlorination going too far and furnishing ferric chloride (*q.v.*). Ferrous chloride is better prepared by passing hydrogen chloride over iron at a red-heat. K. A. Hofmann and co-workers said that the reaction is perceptible at  $285^\circ$ , and F. Schmitz recommended a temp. of  $1000^\circ$ . The process is described in several books of laboratory preparations—e.g., H. and W. Biltz, L. Vanino, etc. M. Berthelot said that the reaction is possible because the heat of formation of ferrous chloride is greater than that of hydrogen chloride, but this is not all the story—1, 12, 3. The equilibrium conditions,  $\text{Fe} + 2\text{HCl} \rightleftharpoons \text{FeCl}_2 + \text{H}_2$ , were discussed by F. Isambert, and A. B. Bagdasarian—*vide infra*. L. F. Nilson and O. Pettersson used a platinum tube; F. Girardet, a porcelain tube; and W. Biltz and E. Birk, a vitreous quartz tube. The ferrous chloride appears as a molten mass, which crystallizes on cooling, and at a high enough temp., the product may occur in sublimed plates. V. Meyer purified ferrous chloride by sublimation in an atm. of hydrogen chloride. H. Wolfram said that a part of the iron escapes attack, and G. J. Fowler recommended removing it by means of a magnet. H. Wolfram said that in the sublimed product iron may be present owing to the temp. being high enough to dissociate some of the chloride. E. Kohn-Abrest added that the product may contain some ferric chloride. The process was also described by H. and W. Biltz, A. Geuther and E. Forsberg, W. Hampe, E. Diepschlag, F. Huttner, A. S. Miller, and A. E. Nordenskjöld. J. Meyer and R. Backa obtained ferrous chloride accompanied by vanadium dichloride by the action of hydrogen chloride on ferrovanadium at  $300^\circ$  to  $400^\circ$ . H. Moissan obtained ferrous chloride by the action of hydrogen chloride on iron carbide at  $600^\circ$ ; the Badische Anilin- und Sodafabrik, by its action on chromite; and F. Bullheimer, and A. C. Knowles, on ferruginous clays.

J. S. F. Pagenstecher prepared ferrous chloride by heating iron filings with an excess of ammonium chloride. A. W. F. Rogstadius added that a trace of ferric

chloride is also formed. The process was examined by J. Fischler, H. Hampel, H. Hampel and R. Steinau, K. A. Hofmann and co-workers, A. S. Miller, and J. Thomsen. Ferrous chloride is formed when various chloride vapours act on iron at an elevated temp.—*e.g.*, sodium chloride:  $\text{Fe} + 2\text{NaCl} \rightleftharpoons \text{FeCl}_2 + 2\text{Na}$  (L. Hackspill and R. Grandadam); aluminium chloride  $3\text{Fe} + 2\text{AlCl}_3 \rightleftharpoons 3\text{FeCl}_2 + 2\text{Al}$  (H. St. C. Deville); carbon tetrachloride (E. Berger); carbonyl chloride (W. Heap and E. Newbery); silicon tetrachloride (E. Vigouroux, and C. Pape); phosphorus trichloride (A. Granger); phosphorus pentachloride:  $\text{PCl}_5 + \text{Fe} \rightleftharpoons \text{FeCl}_2 + \text{PCl}_3$  (E. Baudrimont, and H. Goldschmidt); phosphoryl chloride (B. Reinitzer and H. Goldschmidt); sulphur monochloride (P. Nicolardot); and thionyl chloride (K. Ott, and H. B. North and A. M. Hageman).

M. Berthelot discussed the formation of ferrous chloride by the action of chlorine on ferrous oxide; H. St. C. Deville, by the action of hydrogen chloride on ferrous oxide:  $4\text{FeO} + 2\text{HCl} = \text{Fe}_3\text{O}_4 + \text{FeCl}_2 + 2\text{H}$ ; and G. Rauter, by the action of silicon tetrachloride in a sealed tube at  $370^\circ$  to  $380^\circ$ . H. St. C. Deville also obtained ferrous chloride by the action of hydrogen chloride on strongly-heated ferric oxide; J. B. Moyer, by the action of hydrogen chloride on ferric oxide at  $200^\circ$  when much volatile ferric chloride is formed—F. A. Gooch and F. S. Havens said 90 to 95 per cent.

F. Wöhler obtained ferrous chloride by heating ferric chloride in hydrogen, but, added E. Péligot, at not too high a temp. or the ferrous chloride which is formed will be reduced to the metal. The process was discussed by A. S. Miller, and H. Wolfram. A. B. Bagdasarian recommended heating a mixture of ferric chloride and powdered iron in an atm. of hydrogen and hydrogen chloride (1 : 1). P. Fireman heated a mixture of ferric chloride and ammonium chloride in a sealed tube at  $400^\circ$  to  $420^\circ$ . L. E. Jonas, and A. Benrath exposed an ethereal soln. of ferric chloride to light and obtained ferrous chloride as a white scaly powder; A. W. Ralston and J. A. Wilkinson obtained it as a white precipitate from a soln. of ferric chloride in liquid hydrogen sulphide at ordinary temp.; and V. Thomas, by the action of nitric oxide on ferric chloride:  $\text{FeCl}_3 + \text{NO} = \text{NOCl} + \text{FeCl}_2$ . V. Thomas also observed that the complex  $\text{FeCl}_2 \cdot \text{NO}$  yields ferrous chloride when heated in a neutral atm. Ferric chloride is reduced to ferrous chloride by numerous other reagents. H. E. Williams passed an electric current of low current density through a dil. ethereal soln. of ferric chloride, and observed the formation of ferrous chloride at the cathode.

Numerous compounds of iron yield ferrous chloride when treated with chlorine, hydrogen chloride or chlorides. E. Kothny, and C. F. Prutton observed its formation in the chloridizing roast of pyrites; W. S. Millar, by the action of chlorine on mixtures of ferric oxide and sulphur or sulphur compounds. A. P. Brown obtained it by the action of hydrogen chloride on pyrites; and S. I. Levy and G. W. Gray, by the action of ferric chloride on pyrites at  $500^\circ$  to  $1000^\circ$ , thus  $2\text{FeCl}_3 + \text{FeS}_2 = 3\text{FeCl}_2 + 2\text{S}$ , or the action of chlorine at  $700^\circ$  to  $800^\circ$ :  $\text{FeS}_2 + \text{Cl}_2 = \text{FeCl}_2 + 2\text{S} + 46.5 \text{ Cals.}$ —at this temp. many foreign chlorides are volatilized; the reaction sets in at about  $250^\circ$ . Ferrous chloride is formed by the action of the vapour of chloroform on ferrous sulphate (A. Conduché); the reaction begins at  $300^\circ$ ; by the action of iron carbonyl on a soln. of mercuric chloride in acetone (H. Hock and H. Stuhlmann); by the photochemical decomposition of iron chlorocarbonyl,  $\text{Fe}(\text{CO})_4\text{Cl}_2$  (W. Hieber and G. Bader); and by the action of titanium tetrachloride on ferrous carbonate or titanate (C. Friedel and J. Guérin).

F. A. C. Gren, J. Davy, E. L. Schubarth, and T. Graham obtained the anhydrous salt by heating hydrated ferrous chloride. J. J. Berzelius heated the hydrate in a retort, and after the evolution of water, hydrogen chloride, and ferric chloride had ceased, raised the temp. to a white-heat to volatilize the ferrous chloride. N. Costachescu and G. Spacu recommended dehydrating the hydrate in an atm. of carbon dioxide; W. Biltz and G. F. Hüttig, in an atm. of hydrogen chloride at  $120^\circ$  to  $130^\circ$ ; and A. Geuther and E. Forsberg, with ammonium chloride—in the latter

case, a soln. of hydrated ferrous chloride was mixed with ammonium chloride, dried, and heated in the absence of air.

**The hydrates of ferrous chloride.**—A soln. of ferrous chloride is obtained by dissolving iron, or ferrous oxide, hydroxide or carbonate in hydrochloric acid in the absence of air. H. Hess said that if conc. acid be used with iron, crystals separate from the soln. and these dissolve in water with decrepitation and the

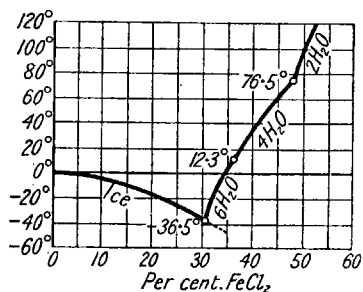


FIG. 560.—The Solubility of Ferrous Chloride in Water.

evolution of an inflammable gas—presumably derived from the carbide in the iron. The ferrous compounds are not easily obtained quite free from oxidation products, so that the soln. may be contaminated with ferric chloride. H. Meyer accordingly recommended filtering the soln. through a column of iron turnings in an atm. of carbon dioxide. J. H. Long discussed the preparation of a soln. free from acid; and R. Phillips recommended adding barium chloride to a soln. of ferrous sulphate in a neutral atm. The preparation of soln. of ferrous chloride from various by-products was described by F. J. R. Carulla, C. Mené, and

R. H. Muench. The evaporation of the aq. soln. furnishes various hydrates. According to A. Reimann, the aq. soln. sat. at room temp. contains 38.1 per cent.  $\text{FeCl}_2$ ; J. T. Dunn found 37.53 per cent. at  $15.5^\circ$ ; H. E. Boeke, 39.8, 41.6, and 42.2 per cent. respectively at  $22.8^\circ$ ,  $38.0^\circ$ , and  $43.2^\circ$ ; and Y. Osaka and T. Yaginuma, 39.61 per cent. at  $25^\circ$ . Observations were made by F. Jahn, "Abl.," and C. F. Wenzel. A. Étard's data for the percentage solubility,  $S$ , are :

	$10^\circ$	$20^\circ$	$30^\circ$	$50^\circ$	$60^\circ$	$80^\circ$	$100^\circ$	$120^\circ$
$S$	39.2	40.7	42.2	45.2	47.0	50.0	51.4	51.8
	$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$					$\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$		

The following is a selection from F. Schimmel's data, plotted in Fig. 560 :

	$-9^\circ$	$-36.5^\circ$	$-20^\circ$	$-3.0^\circ$	$12.3^\circ$	$25.0^\circ$	$76.5^\circ$	$86.0^\circ$	$117.5^\circ$
$S$	14.5	30.4	31.0	32.6	37.6	39.2	47.4	47.7	50.4
	Ice		$\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$		$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$		$\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$		

so that the eutectic temp. with the hexahydrate is  $-36.5^\circ$ , with soln. containing 30.4 per cent. of  $\text{FeCl}_2$ . The transition temp. for the hexahydrate and tetrahydrate is  $12.3^\circ$ ; and for the tetrahydrate and dihydrate,  $76.5^\circ$ . H. E. Boeke gave  $72.2^\circ$  to  $72.6^\circ$ ; and R. Kremann and F. Noss,  $65.2^\circ$ . H. E. Boeke found that there is an increase in vol. at the tetrahydrate and dihydrate transition temp., and the transition temp. is lowered in the presence of sodium or magnesium chloride. J. Eggert and J. Reitstötter discussed the relation between the transition temp. and the water of crystallization and number of atoms in the molecule.

J. Thomsen suggested that there is probably a **hexahydrate**,  $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$ , and P. Pfeiffer represented the formula  $[\text{Fe}(\text{H}_2\text{O})_6]\text{Cl}_2$ —*vide infra*. This hydrate was isolated by H. Lescœur in the form of pale green, unstable crystals, by cooling a neutral, sat. aq. soln. He thought that since other observers had always obtained a tetrahydrate, his hexahydrate must be produced in neutral soln. under conditions where in the acidic soln. the tetrahydrate is formed. P. Sabatier, indeed, denied the existence of the hexahydrate. G. Agde and F. Schimmel, however, showed that the discrepancy is not due to the use of a neutral or acidified soln., but is rather an effect of temp. The transition point,  $12.3^\circ$ , is very near the ordinary temp. of a room, in some cases one hydrate is formed, in other cases, the other hydrate. All depends on the temp. of the soln. H. Lescœur recommended cooling a neutral soln. of ferrous chloride, sat. at  $10^\circ$ , down to  $-15^\circ$ . There is a tendency to under-cooling. G. Agde and F. Schimmel observed that when hydrogen

chloride is passed into a cold sat. soln. of the gas, the absorption of the hydrogen chloride raises the temp. of the soln. above the transition temp., thus giving rise to the idea that the hexahydrate is not formed in acidic soln. The crystals obtained by R. Boyle, J. J. Berzelius, E. L. Schubarth, L. J. Thénard, P. A. von Bonsdorff, T. Graham, and A. Reimann by evaporation and cooling an aq. soln. of the salt, were the **tetrahydrate**,  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ , which A. Werner represented by the co-ordination formula  $[\text{Fe}(\text{H}_2\text{O})_4]\text{Cl}_2$ . The subject was discussed by R. Reinicke. H. Lescœur obtained it by passing hydrogen chloride into a sat. soln. of ferric chloride; the necessary condition is that the temp. of the soln. must exceed  $12.3^\circ$  as pointed out by G. Agde and F. Schimmel, Fig. 560; A. Benrath found that the tetrahydrate is deposited when a soln. of hydrated ferric chloride in methyl alcohol is exposed to sunlight, and H. E. Williams by the electrolysis of an ethereal soln. of hydrated ferric chloride. H. Lescœur obtained the **dihydrate**,  $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ , by dehydrating the tetrahydrate at  $70^\circ$  to  $90^\circ$ . The conditions of existence are shown in F. Schimmel's diagram, Fig. 560. H. E. Boeke found that the dihydrate separates from a sat. soln. at  $72.6^\circ$ , and in the presence of magnesium chloride, at  $43.2^\circ$ . R. Kremann and F. Noss' value,  $65.2^\circ$ , for the transition temp. is low. P. Sabatier said that it is formed when the tetrahydrate is kept for a few months over sulphuric acid in vacuo at  $20^\circ$ . The observations of H. Lescœur, and P. Sabatier on the formation of the dihydrate by passing hydrogen chloride into an aq. soln. of ferrous chloride are explained by the need for allowing for the raising of the temp. of the soln. when the gas is introduced, and the need for keeping the crystallizing soln. above the transition temp.,  $76.5^\circ$ . L. E. Jonas found that an ethereal soln. of hydrated ferric chloride deposits the dihydrate; E. Puxeddu, that an ethereal soln. of anhydrous ferric chloride deposits the dihydrate in sunlight; and A. Benrath, that a similar result is obtained with a soln. in absolute ethyl alcohol. F. Reitzenstein obtained the dihydrate by keeping the complex  $\text{FeCl}_2 \cdot 3\text{Py} \cdot 2\text{H}_2\text{O}$  over conc. sulphuric acid for some months. H. Chandra found that molten  $\text{Fe}_3\text{Cl}_8 \cdot 10\text{H}_2\text{O}$  deposits crystals of the dihydrate. H. Lescœur observed that vap. press. measurements indicate the formation of a *monohydrate*, at a temp. exceeding  $120^\circ$ ; and the observations of K. Honda and T. Ishiwara on the magnetic susceptibility indicate that the monohydrate is formed at  $161^\circ$ , and that at  $220^\circ$ , this passes into the anhydrous chloride.

**The physical properties of ferrous chloride.**—The anhydrous chloride was described by J. Davy, H. Davy, J. S. F. Pagenstecher, A. E. Nordenskjöld, V. Meyer, W. Hampe, and F. Girardet as forming white plates resembling talc, or anthracene; and, according to C. F. Rammesberg, they have a mother-of-pearl lustre. L. F. Nilsson and O. Pettersson said that the molten salt solidifies to a radiating crystalline mass the colour of siderite. H. de Senarmont said that the tabular **crystals** are six-sided, optically uniaxial, and negative; A. E. Nordenskjöld said that the plates belong to the hexagonal system. G. Bruni and A. Ferrari added that the crystals are rhombohedral with a space-lattice like the chlorides of magnesium, cadmium, and manganese; and axial ratio is  $a : c = 1 : 2.45$ ; and  $a = 7.155 \text{ \AA}$ , and  $c = 17.52 \text{ \AA}$ . S. Surawicz discussed the symmetry of the crystals of ferrous chloride and its hydrates; and W. Klemm, the energy of the crystal lattice. H. Lescœur said that the crystals of the hexahydrate are pale green; and L. J. Thénard, J. J. Berzelius, and E. L. Schubarth also said the crystals of the tetrahydrate are pale green; and A. Benrath's crystals from methyl alcohol soln., were bluish-green. P. A. von Bonsdorff added that the light-blue crystals of the tetrahydrate become grass-green on exposure to air, and then acquire a surface film coloured yellowish-brown. According to A. Johnsen, the crystals are colourless when viewed by transmitted light parallel to the (100)-face, and pale bluish-green when viewed parallel to the (010)-face. J. Schabus added that the crystals are rarely transparent, mostly translucent. They are rather brittle, with a conchoidal or splintery fracture; the taste appears at first to be piercing, then sweet and astringent, and then metallic. F. A. Flückiger said that the taste is saline, and not bitter like that of ferric chloride.



According to E. L. Schubarth, P. A. von Bonsdorff, A. Reimann, and J. Schabus, the crystals are rhombic prisms, octahedra, or, if crystallized rapidly, plates. A. Johnsen calculated for the rhombic crystals from J. Schabus' measurements, the axial ratios  $a : b : c = 1.1946 : 1 : 1.6354$ ; B. Gossner calculated from A. Johnsen's measurements, on the assumption that the crystals are monoclinic,  $a : b : c = 1.1844 : 1 : 1.6358$ , and  $\beta = 111^\circ 11'$ . O. Lehmann studied the twinning of the monoclinic crystals. A. Johnsen said that the twinning occurs about the (001)-plane; and that the cleavage on the (001)-face is perfect, whilst that on the (111)-face is imperfect. B. Gossner added that the optical character is negative, and that the optic axial angle  $2E = 65^\circ$  nearly. L. E. Jonas described the crystals of the dihydrate as green; H. E. Boeke, pale green or colourless; and E. Puxeddu, white. O. Lehmann said that the needle-like crystals are monoclinic, with frequent **twinning**; H. E. Boeke observed that the **birefringence** is strong, the twinning may be cruciform, that the monoclinic crystals have  $\beta = 130.5^\circ$ , and that they are probably isomorphous with dihydrated manganous chloride. O. Lehmann discussed the solid soln. with ammonium chloride.

V. Meyer found the **vapour density** of anhydrous ferrous chloride in an atm. of hydrogen chloride at a yellow-heat to be 6.38 to 6.67 (air unity). These numbers are between the values required for a molecular weight of 126.8 for  $\text{FeCl}_2$  and 253.6 for  $\text{Fe}_2\text{Cl}_4$ . A. Ladenburg, and J. Dewar and A. Scott also obtained results showing that the vapour corresponds with an equilibrium mixture  $\text{Fe}_2\text{Cl}_4 \rightleftharpoons 2\text{FeCl}_2$ . According to L. F. Nilson and O. Pettersson, the dissociation is complete between  $1300^\circ$  and  $1500^\circ$  for the vapour density between  $1300^\circ$  and  $1400^\circ$  is 4.34, and between  $1400^\circ$  and  $1500^\circ$ , 4.29 when the theoretical value for  $\text{FeCl}_2$  is 4.375. A. Werner and W. Schmujiuff found that in a boiling soln. of pyridine the mol. wt. is 110 corresponding with the value 126 calculated for the simple formula  $\text{FeCl}_2$ . J. Schröder, however, could not confirm this since he always obtained a raising and not a lowering of the b.p. H. Goldschmidt and K. L. Syngros calculated from the f.p. of aq. soln. having 0.205 to 1.999 grm.  $\text{FeCl}_2$  per 100 grms. of water, values for the mol. wt. ranging from 44.3 to 48.2. Analogous results were obtained by W. Biltz, and R. Peters. This is taken to mean that the salt is ionized  $\text{FeCl}_2 \rightleftharpoons \text{Fe}^{++} + 2\text{Cl}^-$  in aq. soln. The potential measurements of S. Labendzinsky show that the conc. of the  $\text{Fe}^{++}$ -ions in  $N\text{-FeCl}_2$  at  $18^\circ$  is about 2.5 times as great as in  $0.1N\text{-FeCl}_2$ ; and O. Baudisch and P. Mayer said that the evidence indicates that complexes are formed in aq. soln. such that  $2\text{FeCl}_2 \rightleftharpoons \text{Fe}^{++} + \text{FeCl}_4^{--}$ . H. Lessheim and co-workers discussed the co-ordination number of iron in  $[\text{FeCl}_4]^{--}$ , and the electronic configuration of the  $\text{Fe}^{++}$ -ion.

E. Filhol gave 2.528 for the **specific gravity** of the anhydrous chloride; and J. P. Grabfield, 2.988 at  $17.9^\circ$ . W. Biltz and E. Birk obtained for the salt which had been melted in an atm. of hydrogen chloride, 3.162 at  $25^\circ/4^\circ$ . A. Ferrari and co-workers calculated from the lattice constants 3.254. A. Balandin obtained 2.985 by calculation from an empirical relation between the heat of formation and the at. vol. E. Filhol gave 1.926 for the sp. gr. of the tetrahydrate; J. Schabus, 1.937; and A. Johnsen, 1.96; and G. Heyne obtained 2.358 for the sp. gr. of the dihydrate. H. Becquerel found the sp. gr. of soln. with 6.6, 13.2, 26.41, and 52.83 grms. of  $\text{FeCl}_2$  per 100 c.c. of soln. at about  $16^\circ$ , the respective values 1.0548, 1.1093, 1.2141, and 1.4331. A. Heydweiller obtained for soln. with 0.25, 1.0, 2.0, and 3.0 mols of  $\text{FeCl}_2$  per litre at  $18^\circ/4^\circ$ , the respective values 1.02779, 1.1085, 1.2122, and 1.3130; and W. Biltz and J. Meyer, for soln. with 0.0256, 0.08775, 0.3050, and 0.3994 mol of  $\text{FeCl}_2$  per litre, the respective sp. gr. 1.003, 1.012, 1.043, and 1.056. Observations were also made by F. W. J. Clendinnen, G. T. Gerlach, and G. Quincke. J. T. Dunn found that the sp. gr. is almost proportional to the percentage proportion of  $\text{FeCl}_2$  in soln. since he obtained for soln. with  $\text{FeCl}_2$ -per cent. of the anhydrous salt at  $15.5^\circ$ :

$\text{FeCl}_2$	5.40	10.47	15.24	19.68	23.86	27.75	31.39	34.80	37.33	per cent.
Sp. gr.	1.05	1.10	1.15	1.20	1.25	1.30	1.35	1.40	1.44	

W. Biltz, and W. Biltz and E. Birk found the **molecular volume** of anhydrous ferrous chloride to be 40·10 at 25°, and that the formation of the salt from its elements is attended by a small dilation; and J. J. Saslawsky, and W. Klemm came to the same conclusion. F. Ephraim and co-workers also studied the mol. vol.; H. H. Stephenson, the relation between the mol. vol. and the contraction; F. Teltscher, and R. Reinicke, the relation between the mol. vol. and the structure. S. Surawicz, and A. Balandin discussed the mol. vol. of the tetrahydrate; and C. A. Valson examined the contraction which occurs when ferrous chloride is dissolved in water. J. Schabus gave for the **hardness** of the crystals of the tetrahydrate 2·0 on Mohs' scale.

T. Graham made observations on the **rate of diffusion** of ferrous chloride in aq. soln.; and J. C. Graham found the diffusion coeff. in 2 to 5 per cent. soln., at 14° to 16°, to be 0·583 sq. cm. per day—*i.e.* nearly twice as fast as is the case with ferrous sulphate—and the coeff. is not much affected by variations of concentration between these limits. T. Redwood studied the diffusion of the salt through a membrane, and E. Deiss and G. Schikorr observed that no hydrolysis occurs during the diffusion. The **surface tension** of the soln. was studied by G. Wertheim; the effect of a magnetic field on the ascent of the soln. in capillary tubes, by G. Wertheim, G. Quincke, and O. Liebknecht and A. P. Wills; and Z. H. Skraup and co-workers, the ascent of soln. of the salt in filter-paper.

H. Goldschmidt and K. L. Syngros found the **lowering of the freezing-point** of aq. soln. with 0·205, 0·928, 1·531, and 1·999 grms. FeCl<sub>2</sub> per 100 grms. of water to be respectively 0·088°, 0·374°, 0·609°, and 0·788°; W. Biltz and J. Meyer found for soln. with 0·0256, 0·08775, 0·3050, and 0·3994 mol of FeCl<sub>2</sub> per litre, the respective values 0·133°, 0·452°, 1·614°, and 2·169°, corresponding with the mol. depressions 52·0, 51·5, 52·9, and 54·3 respectively. R. Peters showed that soln. with 0·5, 0·25, 0·125, and 0·0625 eq. FeCl<sub>2</sub> per litre gave values corresponding with the mol. wts. 45·7, 44·8, 45·5, and 43·1 respectively; and with the percentage ionizations 93, 95, 91, and 98 respectively. All this is in agreement with a high degree of ionization:  $\text{FeCl}_2 \rightleftharpoons \text{Fe}^{++} + 2\text{Cl}'$  of the salt in aq. soln. N. Sasaki studied the effect of potassium iodide, and ferric chloride on the lowering of the f.p. of aq. soln. of ferrous chloride; and W. Biltz and J. Meyer, the relation between the mol. lowering of the f.p., and the heat of soln.

J. Davy, H. Davy, and W. Hampe observed that anhydrous ferrous chloride melts at a red-heat. K. Honda and T. Ishiware gave 670° for the **melting-point**, and A. Ferrari and co-workers 673° to 674°. A. Ferrari discussed the relation between the m.p. and the space-lattice. C. G. Maier observed the **vapour pressure**, *p* mm., of anhydrous ferrous chloride at

	699°	762·4°	807·6°	859·7°	908·7°	951·0°	994·9°
<i>p</i>	12·2	36·3	57·4	126·8	230·5	371·4	593·0

No **thermal dissociation** was observed at temp. up to 1000°, although H. Wolfram said that during the sublimation of ferrous chloride, some ferric chloride is formed by the partial decomposition of the ferrous chloride. V. Meyer, and V. and C. Meyer represented the action  $3\text{FeCl}_2 = 2\text{FeCl}_3 + \text{Fe}$ . V. Meyer added that no dissociation occurs if the salt be sublimed in an atm. of hydrogen chloride; and L. F. Nilson and O. Pettersson observed no decomposition at 1300° to 1500° in an atm. of hydrogen chloride. P. A. von Bonsdorff found that the crystals of the tetrahydrate effloresce rapidly forming a white powder when they are kept over conc. sulphuric acid; and P. Sabatier observed that when kept for 3 months in vacuo, over conc. sulphuric acid, at 20°, the dihydrate is formed. A. Johnsen said that the crystals of the tetrahydrate become turbid at 40°. A. Reimann observed that the tetrahydrate "fuses in its water of crystallization"; but, according to A. Étard, the tetrahydrate does not melt when heated, but passes into the dihydrate above 90°, and loses its water of crystallization at 120°; A. Gorgeu, however, observed that when heated in an atm. of moist hydrogen, the tetrahydrate melts and it then

contains anhydrous ferrous chloride along with some ferrous oxychloride. According to J. J. Berzelius, when the tetrahydrate is heated in a retort, it first melts in its water of crystallization, then decomposes with the evolution of hydrogen chloride, water, and the vapour of ferric chloride, and when the temp. attains the softening-point of glass, white or colourless ferrous chloride sublimes, and a basic ferrous chloride remains in the retort. The sublimate is yellow owing to the presence of a little ferric chloride. H. Lescœur observed that the **dissociation pressure** of the tetrahydrate is 120 to 130 mm. at  $70^\circ$ ; and that the press. falls abruptly to 2 mm. at  $70^\circ$  as the tetrahydrate passes into the dihydrate. The vap. press. of the dihydrate at  $90^\circ$ ,  $110^\circ$ , and  $125^\circ$  is 30, 75, and 188 mm. respectively. The dissociation press. falls from about 130 mm. at  $120^\circ$  to about 17 mm. as the dihydrate passes into the monohydrate; and the dissociation press. of the monohydrate is about 55 mm. at about  $155^\circ$  when it passes into the anhydrous chloride. H. Lescœur observed the vap. press.,  $p$  mm., of sat. aq. soln. of ferrous chloride to be:

	$40^\circ$	$50^\circ$	$60^\circ$	$70^\circ$	$80^\circ$
$p$	30	56	88	127	177 mm.

and for the mono- and di-hydrates:

	$90^\circ$	$100^\circ$	$110^\circ$	$120^\circ$	$125^\circ$	$155^\circ$
$p$	30	48	75	130	188	55
	$2\text{H}_2\text{O}$					$\text{H}_2\text{O}$

G. Tammann found the lowering of the vap. press.,  $\delta p$  mm., of soln. of 4.03, 24.05, 51.90, and 90.54 grms. of  $\text{FeCl}_2$  in 100 grms. of water to be respectively  $\delta p=10.3$ , 79.9, 200.1, and 341.8 mm. Observations on the subject were made by M. Prud'homme.

J. Davy, and H. Davy said that anhydrous ferrous chloride does not volatilize at the softening temp. of glass, but J. J. Berzelius obtained marked **volatilization** at this temp., and V. Meyer said that it volatilizes slowly at a red-heat, and rapidly at a yellow-heat. L. F. Nilson and O. Pettersson observed a rapid volatilization of the salt in an atm. of hydrogen chloride between  $1300^\circ$  and  $1500^\circ$ . C. G. Maier extrapolated his vap. press. data, and obtained  $1023.4^\circ$  for the **boiling-point** of anhydrous ferrous chloride; and calculated 32.11 Cals. per mol for the heat of vaporization at  $1023^\circ$  and 1 atm. press., and at  $674.4^\circ$  and 0.01 atm. press. R. Kremann and F. Noss, and F. Schimmel said that a sat. soln. with 50.4 per cent. of  $\text{FeCl}_2$  boils at  $117.5^\circ$ .

P. A. Favre and J. T. Silbermann gave for the **heat of formation** of anhydrous ferrous chloride,  $(\text{Fe}, \text{Cl}_2)=49.651$  Cals., but, according to J. Thomsen, this datum is too low, owing to an incorrect value for the heat of soln. having been employed in the calculation. J. Thomsen gave 82.05 Cals.; M. Berthelot, 82.20 Cals.; W. Biltz and C. Fendius, 82 Cals.; and K. Jellinek and R. Koop, 69.13 Cals. J. Thomsen also gave  $(2\text{FeCl}_3, \text{Fe})=54.07$  Cals., and M. Berthelot, 54.6 Cals. J. Thomsen gave  $(\text{Fe}_{\text{solid}}, \text{Cl}_2, 4\text{H}_2\text{O}_{\text{liq.}})=97.20$  Cals. at  $18^\circ$ ;  $(\text{FeCl}_2, 4\text{H}_2\text{O}_{\text{liq.}})=15.15$  Cals. at  $18^\circ$ ; and P. Sabatier gave  $(\text{FeCl}_2, 2\text{H}_2\text{O}, 2\text{H}_2\text{O}_{\text{solid}})=2.52$  Cals. at  $20^\circ$ , and  $(\text{FeCl}_2, 2\text{H}_2\text{O}_{\text{solid}})=6.40$  to  $6.92$  Cals. T. Andrews gave for the heat of formation of ferrous chloride in soln.  $(\text{Fe}, \text{Cl}_2, \text{Aq.})=99.1$  Cals.; J. Thomsen, 102.06 Cals.; and M. Berthelot, 99.95 Cals. According to J. Thomsen, P. A. Favre and J. T. Silbermann's value, 53.35 Cals., is too low. J. Thomsen also gave  $(\text{Fe}, 2\text{HCl Aq.})=23.42$  Cals.;  $(2\text{FeCl}_3 \text{Aq.}, \text{Fe})=44.41$  Cals.; and M. Berthelot, 44.6 Cals. The subject was discussed by E. Rabinowitsch and E. Thilo, and O. Schütz and F. Ephraim. J. Thomsen gave  $\{\text{Fe}, 2(\text{HCl}+50\text{H}_2\text{O})\}=21.31$  Cals. J. Thomsen stated that the heats of soln. of iron in hydrochloric, hydrobromic, and hydriodic acids are nearly the same. T. W. Richards and co-workers observed  $\{\text{Fe}, n(\text{HCl}+8.8\text{H}_2\text{O})\}=20.55$  Cals.; and  $\{\text{Fe}, 2(\text{HCl}+200\text{H}_2\text{O})\}=20.8$  Cals. J. Thomsen gave for the **heat of neutralization** of ferrous hydroxide by hydrochloric acid,  $(\text{Fe}(\text{OH})_2, 2\text{HCl Aq.})=21.39$  Cals., and he added that an earlier determination by P. A. Favre and J. T. Silbermann is too low; M. Berthelot obtained

21.4 Cals. for the heat of neutralization with 0.25*N*-HCl. According to M. Berthelot, the action of 2KOH on (FeCl<sub>2</sub>.Aq., H<sub>2</sub>SO<sub>4</sub> dil. soln.) = 1.1 Cals.; and on (FeSO<sub>4</sub>.Aq., 2HCl dil. soln.) = 2.5 Cals. J. Thomsen found for the **heat of solution**, (FeCl<sub>2</sub>.Aq.) = 17.9 Cals. at 18.2°, and he added that an earlier determination by P. A. Favre and J. T. Silbermann is too low. J. Thomsen gave 2.75 Cals. for the heat of soln. of 16.58 grms. of the tetrahydrate in about 600 grms. of water at 19.3°; P. Sabatier gave (FeCl<sub>2</sub>.4H<sub>2</sub>O, 600H<sub>2</sub>O) = 3.32 Cals. at 17.5°; (FeCl<sub>2</sub>.Aq.) = 2.7 Cals.; (FeCl<sub>2</sub>.2H<sub>2</sub>O, 1000H<sub>2</sub>O) = 8.72 Cals. at 20°; and (FeCl<sub>2</sub>.2H<sub>2</sub>O, 300 to 600 H<sub>2</sub>O) = 8.7 Cals. at 20°. O. Schütz and F. Ephraïm discussed the relations between the heat of formation and the mol. vol.; and F. Braun, and G. Beck, the **free energy** of formation of ferrous chloride; G. Devoto and A. Guzzi gave 40,200 cals. at 700°; 37,100 cals. at 750°; 32,500 cals. at 800°; and 27,150 cals. at 850°. G. Beck, and W. Herz calculated values for the **entropy** and vibration frequency of FeCl<sub>2</sub>. R. Audubert studied the energy of the reaction Fe<sup>++</sup> → Fe<sup>+++</sup>; and M. Randall and M. Frandsen gave -20,310 cals. for the free energy of the ferrous ion. W. Hieber and E. Levy studied the **lattice energy** of the crystals.

G. Limann, and A. Heydweiller measured the **indices of refraction**,  $\mu$ , of aq. soln. of ferrous chloride at 18°; and G. Limann gave for soln. with *C* equivalents of ferrous chloride per litre:

<i>C</i>	0	0.5	1.0	2.0	4.0
$\left\{ \begin{array}{l} H_a\text{-line} \\ D\text{-line} \\ H_\beta\text{-line} \\ H_\gamma\text{-line} \end{array} \right.$	1.33139 1.33322 1.33737 1.34060	1.33849 1.34038 1.34473 1.34805	1.34546 1.34742 1.35199 —	1.35881 1.36092 1.36588 —	1.38448 1.38682 1.39241 —

W. A. Wooster studied the relation between the refractive index and the lattice structure. The **molecular refraction** for Na-light by the  $\mu^2$ -formula is 19.23 at 18°; and A. Heydweiller obtained for very dil. soln. to soln. with 4 eq. of FeCl<sub>2</sub> per litre values ranging from 19.34 to 19.12—average 19.23. Let  $\delta\mu$  denote the difference between the value of  $\mu$  for a soln. of conc. *C* eq. per litre, and water, G. Limann obtained for *D*- and *H<sub>a</sub>*-light, at 18°, the dispersion  $10^5(\delta\mu_D - \delta\mu_a)/C = 14.4$ ; and for *H<sub>\beta</sub>*- and *D*-light,  $10^5(\delta\mu_\beta - \delta\mu_D)/C = 38.6$ . A. Heydweiller also studied this subject.

J. S. F. Pagenstecher observed that aq. soln. of anhydrous ferrous chloride are at first colourless, but they soon become green when exposed to the air; and A. Étard observed that if a green sat. soln. be heated in a sealed tube at 240°, it becomes colourless. H. M. Vernon studied this subject. W. J. Russell and W. J. Orsman said that soln. of ferrous chloride in hydrochloric acid show no absorption bands in the visible **spectrum**. J. S. Anderson found the **molecular extinction coefficient** *k* of soln. with *C* = 4 mols per litre:

$\lambda$	4340	5470	6250	7460	8370	9680	11,750	1300 A.
<i>k</i>	0.75	0.025	0.042	0.115	0.17	0.89	1.00	0.84

and for the effect of concentration, with  $\lambda = 4530$  A., and 6530 A.:

4530 A.					6530 A.				
<i>C</i>	4.0	2.0	1.0	0.5	4.0	2.0	1.0	0.5	
<i>k</i>	0.39	0.18	0.16	0.22	0.057	0.067	0.082	0.12	

Observations on the subject were also made by J. von Koczkas, and R. A. Houston and C. Cochrane. According to R. Zsigmondy, the percentage **transmission of heat rays**, *H*, from an Argand burner through layers 9.5 mm. thick of hydrochloric acid soln. of *C* mols of FeCl<sub>2</sub> per litre, is as follows:

<i>C</i>	2	1	0.5	0.25	0.125	0.0625	0.03125	0
<i>H</i>	1.16	1.85	4.06	6.73	8.95	10.31	10.93	12.2 per cent.

and with different ferrous salts, the results are the same with soln. containing the same proportion of ferrous iron. The high degree of absorption makes the soln. suitable for filtering out the heat rays. S. M. Karim and R. Samuel studied

the **absorption spectrum**. A. Byk and H. Jaffe found that soln. containing 2.53, 1.27, 0.51, and 0.12 grms. of  $\text{FeCl}_2$  in 100 c.c. of dil. hydrochloric acid, in layers 1 cm. thick, have limits of absorption with ultra-violet light of wavelength 2735, 2566, 2351, and 2322 respectively. M. N. Saha and S. C. Deb examined the absorption spectrum of the vapour at  $1000^\circ$  to  $1400^\circ$ . O. Stelling, and S. Aoyama and co-workers studied the absorption of the K-series of the **X-ray spectrum** by anhydrous and tetrahydrated ferrous chloride; and A. Hébert and G. Raynaud, the absorption of X-rays by aq. soln. of ferrous chloride. G. Reboul and E. Bodin found that, unlike ferrous sulphate, ferrous chloride emits no radiations when it is connected with the poles of a battery of 2500 volts. M. E. Verdet showed that the mol. **magnetic rotation** of the plane of polarized light for 16.0 and 28.3 per cent. soln. of ferrous chloride is respectively  $-0.82$  and  $-0.94$ . Observations were also made by E. Becquerel, and O. Schönrock. H. Becquerel found for sodium light with soln. containing 0.5283, 0.2641, 0.1320, and 0.0660 grm. of  $\text{FeCl}_2$  per 100 c.c., at  $15^\circ$  to  $18^\circ$ , the respective sp. gr. 1.4331, 1.2141, 1.093, and 1.0548; the relative magnetic rotation, for the sodium-line, respectively 0.195, 0.765, 0.908, and 0.954, and the respective magnetic rotations  $-1.343$ ,  $-0.701$ ,  $-0.528$ , and  $-0.521$ . F. Allison and E. J. Murphy studied the magneto-optic properties; P. Krishnamurti, the **Raman effect**, and O. Stelling, the **X-ray spectrum**—K-series. G. Dima found that the **photoelectric effect** is greater than it is with ferric chloride; and A. Pochettino, similarly with Hallwachs' effect. G. C. Schmidt examined the nature of the charged particles emitted when the salt is heated, and found them to be of atomic dimensions.

A. C. Becquerel found that with a static **electric discharge**, ferrous chloride passes from the negative to the positive pole. G. C. Schmidt, and H. Querengässer measured the **electrical conductivity** of the iron halides in flames. W. Hampe observed that molten anhydrous ferrous chloride is a good conductor; G. Vicentini measured the eq. electrical conductivity,  $\lambda$  mho, of soln. of ferrous chloride containing  $C$  eq. per litre at  $18^\circ$ , for  $C$  up to 0.0038, and A. Heydweiller for larger values of  $C$ , found:

$C$	.	.	0.00101	0.0038	0.05	1.0	2.0	4.0	6.0
$\lambda$	.	.	76	73	69.5	60.6	48.11	30.84	18.13

Observations were also made by G. Limann; C. Cattaneo, and W. Jufereff measured the molar conductivity; and R. Peters, F. Förster, and O. Mustad, the sp. conductivity. G. Limann discussed the relation between the electrical conductivity and light refraction of the soln. For the **ionization** of the soln., *vide supra*, lowering of the f.p. of aq. soln. A. Günther-Schulze discussed the dissociation of the salt in aq. soln. A. Stepniczka-Marinkovic found the **transport number** of the  $\text{Fe}^{++}$ -ion in 0.988*N*-, 0.494*N*-, and 0.172*N*- $\text{FeCl}_2$  to be respectively 0.300, 0.326, and 0.375; by extrapolation, these data gave 0.414 for the transport number at infinite dilution. It was estimated that in 0.172*N*- $\text{FeCl}_2$ , acidified with a little hydrochloric acid, at room temp., the **solvation** of the anion corresponds with 21 mols. of water, and of the cation,  $\text{Fe}^{++}$ , with 60 mols. of water. The subject was studied by G. H. Cartledge; and the electro-deposition of iron from the fused chloride, by A. H. W. Aten and co-workers.

E. Petersen found the **electromotive force** of the cell  $C | 2N\text{-FeCl}_2, 20 \text{ per cent. NaCl} | \text{Zn}$  to be 1.290 volts; and C. Winther studied the e.m.f. of the cell  $\text{Pt} | \text{FeCl}_2, \text{HgCl}_2, \text{Hg}_2\text{Cl}_2 | \text{FeCl}_2, \text{HgCl}_2 | \text{FeCl}_2, \text{HgCl}_2, \text{FeCl}_3 | \text{Pt}$  with different concentrations of the soln. of ferrous chloride. G. Tammann discussed the e.m.f. of the Daniell type of cell with the fused chloride. G. Tammann and E. Jenckel found the effect of a press.,  $p$  kgrms. per sq. cm., on the e.m.f.,  $E$  volt, of a hydrochloric acid soln. of ferrous chloride in the cell  $\text{Pt} | 0.1N\text{-HCl}, \text{FeCl}_2 | 0.1N\text{-HCl}, \text{Hg}_2\text{Cl}_2 | \text{Hg}$ , to be, at  $18^\circ$ :

$p$	.	.	1	100	500	1000	1500	2000
$E$	.	.	0.2816	0.2782	0.2738	0.2705	0.2674	0.2643
$dE/p \times 10^3$	.	.	-34.0	-9.0	-15.6	-11.1	-9.5	-8.7

G. Tammann and H. O. von Samson-Himmelsjerna studied the potential of iron against ferrous chloride. E. Bouty showed that if two iron electrodes dip in soln. of ferrous chloride of the same conc., but different temp., a thermoelectric current is developed, and the warm soln. acts as a positive pole; the e.m.f. is of the order 0.0477 volt; it is proportional to the difference of temp., but is not perceptibly influenced by differences in concentration. L. Riety found a potential difference is developed between a soln. of ferrous chloride passing through a capillary under a press. of 25 atm., and the walls of the tube. The soln. acquires a negative charge. F. Finkelstein measured the polarization capacity of iron in soln. of ferrous chloride. N. Kamayama and K. Takahashi studied the electro-oxidation of the salt. E. Fossatti observed that the electrolysis of a soln. of ferrous chloride is not influenced by a magnetic field; and A. Schükareff observed that in the electrolysis of a soln. of ferrous chloride in a magnetic field of 2000 to 7000 gauss, about the anode, a magnetochemical effect similar to but not identical with the Hall effect occurs. O. Milicka and A. Slama, and R. Fürth measured the **dielectric constants** of soln. of the salt.

M. Faraday found anhydrous ferrous chloride to be paramagnetic. G. Wiedemann observed that the mol. **magnetism** of ferrous chloride is less than that of ferric chloride, and is only a little different from the hydrates or aq. soln. if equal proportions of iron be considered. C. Matteucci said that ferrous chloride shows no remanent magnetization. T. Ishiwara, and K. Honda and T. Ishiwara gave for the **magnetic susceptibility** at different temp.:

	-182.1°	-101.7°	-24.6°	16.5°	193.9°	410.8°	692.3°
$\chi \times 10^6$	449.0	187.4	122.0	101.2	61.4	39.1	22.9

The value of  $\chi$  between  $-190^\circ$  and  $400^\circ$  changes in accord with the formula  $\chi(T + \text{constant}) = \text{constant}$ . H. R. Woltjer and E. C. Wiersma also showed that the formula  $\chi(T - 20.4) = \text{constant}$  applies down to  $-210^\circ$ , but below this temp., the susceptibility is dependent on the intensity of the field, a result opposite to that which holds at a higher temp. O. N. Trapeznikowa and L. W. Shubnikoff studied the Curie point. K. Honda and T. Ishiwara gave for the magnetic moment of a single molecule  $4.67 \times 10^{-20}$ . C. Matteucci found that the tetrahydrate shows no remanent magnetization. T. Ishiwara, and K. Honda and T. Ishiwara gave for the magnetic susceptibility,  $\chi$ , at different temp.:

	-181.2°	-99.6°	-39.3°	19.4°	107.3°	216.1°	400.4°	685.3°
$\chi \times 10^6$	210.0	101.9	76.0	60.1	50.4	46.8	30.8	17.3

When the tetrahydrate is heated, K. Honda and T. Ishiwara said that the water in the substance separates out at four different ranges of temperatures,  $25^\circ$  to  $50^\circ$ ,  $105^\circ$  to  $115^\circ$ ,  $150^\circ$  to  $160^\circ$ , and  $215^\circ$  to  $240^\circ$ . The first small diminution of the weight may be an effect of the moisture, the second is due to the separation of two mols. of water, the third and the fourth are due to the separation of one or both mols. of water.

M. Faraday observed that aq. soln. of ferrous chloride are paramagnetic. C. Matteucci observed no evidence of any remanent magnetization, and no evidence of any enrichment of the soln. in iron salt in the vicinity of a magnetic pole. Observations on the magnetic susceptibility were made by J. Plücker, G. Piaggese, O. Wylach, E. Becquerel, H. Fahlenbrach, E. C. Wiersma, and H. W. Eaton. G. Quincke gave  $89 \cdot 10^{-6}$  at  $19^\circ$ ; J. S. E. Townsend,  $91 \times 10^{-6}$  at  $10^\circ$ , and G. Jäger and S. Meyer,  $61 \times 10^{-6}$  at  $18^\circ$ . The mol. magnetic susceptibilities observed by A. Quartaroli for soln. with a mol of  $\text{FeCl}_2$  in  $v$  litres, at  $18^\circ$ , were:

$v$	10	20	50	100	250	500	750
$\chi \times 10^6$ (mol)	11,841	11,500	11,455	10,944	10,840	10,638	10,496

Observations on the influence of the conc. of the soln. were made by J. Plücker, G. Wiedemann, J. S. E. Townsend, H. Fahlenbrach and E. Vogt, E. Vogt, C. J. Gorter, A. Quartaroli, and P. Théodorides, and the results show that the

mol. magnetic susceptibility decreases slowly with dilution. A. Heydweiller observed very little change in passing from the tetrahydrate to the soln. G. Wiedemann, G. Quincke, and J. S. E. Townsend measured the effect of temp., and the last-named found that the susceptibility falls linearly as the temp. is increased. G. Quincke, H. E. J. G. du Bois, J. S. E. Townsend, R. H. Weber, and A. Heydweiller found that small changes in the magnetic field-strength have very little influence on the susceptibility. H. Fahlenbrach discussed the magnetic moment. A. Quartaroli, L. Pauling and M. L. Huggins, and G. Foëx calculated values for the magneton number.

S. S. Bhatnagar and co-workers observed that paramagnetic iron salts become diamagnetic when adsorbed on charcoal, thus showing that the process of adsorption is more akin to chemical combination than to admixture. According to G. Roasio, the magnetic field exercises an influence on (1) the orientation of the crystals, the angles between axes and lines of force varying with the substance, but being constant for a given compound; and (2) the growth of the crystals, which become elongated in a definite direction, the angles remaining constant, but again varying with the substance.

**The chemical properties of ferrous chloride.**—According to E. Péligot, anhydrous ferrous chloride is reduced to metal when it is heated in dry **hydrogen**; and V. and C. Meyer observed a partial reduction when the chloride is sublimed in hydrogen. W. Spring, and H. Wolfram also observed the reduction of the chloride to the metal. W. Biltz and F. Meyer gave  $\text{FeCl}_3 \cdot \text{Aq.} + \frac{1}{2} \text{H}_2 = \text{FeCl}_2 \cdot \text{Aq.} + \text{HCl} \cdot \text{Aq.} + 10.3 \text{ Cals.}$  F. Schmitz said that the reduction occurs at  $300^\circ$  to  $400^\circ$ ; and A. Smits and co-workers obtained pyrophoric iron by reducing the chloride at  $350^\circ$ . P. Schützenberger thought that a volatile hydrochloride,  $\text{FeHCl}$ , or  $\text{FeCl}_2 \cdot n\text{HCl}$ , is formed, but this has not been confirmed. A. B. Bagdasarjan studied some equilibrium conditions in the reaction  $\text{FeCl}_2 + \text{H}_2 \rightleftharpoons 2\text{HCl} + \text{Fe}$ , with fused ferrous chloride, and found  $K = p_{\text{HCl}}^2/p_{\text{H}_2}$ , and obtained the following values of  $K$  and percentages of hydrogen chloride, and hydrogen in the gases:

	$\text{FeCl}_2 + \text{H}_2$				$\text{Fe} + 2\text{HCl}$	
	$702^\circ$	$800^\circ$	$925^\circ$	$932^\circ$	$725^\circ$	$1005^\circ$
$K$	0.064	0.297	0.767	0.813	0.11	1.63
HCl	22.0	41.6	57.3	58.4	28.2	69.5 per cent.
$\text{H}_2$	78.0	58.4	42.7	41.6	71.8	30.5 „

The breaks in the curve for  $\log K$  and  $T^{-1}^\circ K$  are supposed to be due to allotropic transformations in the iron. K. F. Bonhöffer observed no reaction between ferrous chloride and activated hydrogen. B. Neumann observed that the aq. soln. is not reduced by hydrogen in the presence of platinum.

According to J. L. Gay Lussac, if **oxygen** be passed over molten ferrous chloride, chlorine and ferric oxide are formed; and if the supply of air be restricted, some ferric chloride is produced. *Vide supra* for the oxidation of soln. of ferrous chloride in connection with the oxidation-reduction potential of iron salts. H. Schulze, and S. I. Levy and G. W. Gray represented the reaction of oxygen or dry **air** on heated ferrous chloride:  $12\text{FeCl}_2 + 3\text{O}_2 = 8\text{FeCl}_3 + 2\text{Fe}_2\text{O}_3$ ; and if a small proportion of ferrous chloride is employed, some chlorine is formed, and some ferric chloride is always produced and volatilized when ferrous chloride is so oxidized. S. I. Levy and G. W. Gray found that at  $250^\circ$ , in air—dry or moist—hydrated ferrous chloride rapidly forms ferric oxide and hydrogen chloride. A. Gorgeu obtained crystals of ferric oxide by melting ferrous chloride in air at dull redness, and crystals of ferrosic oxide at a cherry-red-heat; in the latter case, the vapour of ferrous chloride protects the salt from a vigorous attack by oxygen. J. S. F. Pagenstecher observed that when white ferrous chloride is exposed to air, it first becomes matt, then greenish-yellow, and finally reddish-brown. J. Schabus also made some observations on this subject, and H. Wolfram added that anhydrous ferrous chloride is less hygroscopic than ferric chloride. P. A. von Bonsdorff also noted that the light

blue crystals of the tetrahydrate become grass-green on exposure to air, and then acquire a yellowish-brown opaque film; the tetrahydrate is deliquescent, but it effloresces in dry air over  $50^{\circ}$ . P. Nicolardot, and F. Tommasi discussed the nature of the yellowish-brown, hydrated ferric oxide which is formed during the aerial oxidation of ferrous chloride. C. F. Rammelsberg obtained crystals of ferrous oxide by passing air and **water** vapour over red-hot ferrous chloride, and E. A. Parnell, crystals of ferric oxide. H. Frischer said that the reaction is almost complete in 1 to  $1\frac{1}{2}$  hrs. at  $250^{\circ}$ . J. L. Gay Lussac represented the reaction with water vapour:  $3\text{FeCl}_2 + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 6\text{HCl} + \text{H}_2$ . Analogous observations were made by E. A. Parnell, F. Konther, and A. Gautier. H. W. Fischer observed that when a soln. of the chloride is heated in a sealed tube at  $210^{\circ}$ , black plates are deposited. According to H. Precht, the reaction between steam and ferrous chloride at a comparatively low temp., in geological periods, resulting in the formation of hydrogen and ferric oxide, explains the presence of hydrogen in the carnallite deposits of Stassfurt; and E. Erdmann observed that hydrogen is formed when ferrous chloride and water are heated 160 hrs. at  $100^{\circ}$  to  $120^{\circ}$ . H. Precht, and E. Pfeiffer represented the action of water on ferrous chloride or douglasite by  $6\text{FeCl}_2 + 3\text{H}_2\text{O} = 4\text{FeCl}_3 + \text{Fe}_2\text{O}_3 + 3\text{H}_2\text{O}$ . The reaction was studied by H. E. Boeke, and H. Ditz. G. Schikorr found that ferric oxide and iron turnings at room temp. act on water with the evolution of hydrogen; and that water is decomposed by ferrous hydroxide. W. Traube and W. Lange found that ferrous hydroxide in the presence of finely-divided palladium and water, develops hydrogen when heated. R. Phillips observed that when an aq. soln. of ferrous chloride is exposed to air, it is hydrolyzed, and the ferrous hydroxide is oxidized by air to hydrated ferric oxide which is precipitated. The solubility of ferrous chloride in water has been previously discussed—Fig. 560. According to F. Jahn, the hydrolysis is indicated by the reddening of litmus by the aq. soln.; but C. C. Ahlum observed that the aq. soln. is neutral towards methyl orange. J. H. Long found the degree of hydrolysis of  $0.5N\text{-FeCl}_2$  at  $85^{\circ}$ , from its action on the inversion of cane-sugar, to be 0.063 per cent. H. Zocher and W. Heller observed the slow hydrolysis of 0.1 to 8 per cent. soln. of ferrous chloride resulting in the deposition of anisotropic layers. E. Deiss and G. Schikorr said that the degree of hydrolysis is too small to be detected when the soln. diffuses through a membrane. The autoxidation of soln. of ferrous salts was studied by H. Wieland and W. Franke, using sodium acetate and acetic acid as a buffer. Absorption of oxygen follows the unimolecular law. The temp. coeff. of the process is normal, whilst a change from  $p_{\text{H}}=5$  to 7 accelerates the reaction 4- or 5-fold. At  $p_{\text{H}}=5$ , neutral salts have little effect on the rate of autoxidation, although sodium sulphate, possibly owing to its producing complex salts, causes diminution of the reaction velocity to half its previous value. The rate of autoxidation of slightly hydrated ferrous chloride is greater in acetone than in ethyl alcohol or isopropyl alcohol, greater in these solvents than in methyl alcohol, and least in water. R. Thomas and E. T. Williams studied the catalytic influence of nitric oxide on the oxidation of a soln. of ferrous chloride in air, and found the reaction agrees with  $Kt=x(a-\frac{1}{2}x)$ . The rate is proportional to the initial conc. of the ferrous salt; is approximately proportional to the conc. of the catalyst; is independent of the conc. of the hydrochloric acid; and increases 1.8-fold per  $10^{\circ}$  rise of temp. J. C. Duff and E. J. Bills obtained **ferrous hydroxytrichloride**,  $\text{Fe}_2(\text{OH})\text{Cl}_3$ , by the action of hexamethylenetetramine on ferrous chloride; and E. Hayek,  $\text{Fe}(\text{OH})\text{Cl}$ , by boiling a 45 to 50 per cent. soln. of ferrous chloride with iron powder, and washing the product with alcohol. W. Feitknecht found that the space-lattice of  $\text{FeCl}_2 \cdot 4\text{Fe}(\text{OH})_2$  corresponds with alternate layers of the normal salt and the hydroxide. For the action of **hydrogen dioxide**, see the iron peroxides, and ferric chloride. A. K. Goard and E. K. Rideal, D. R. Hale, W. C. Bray and M. H. Gorin, H. Wieland and W. Franke, and S. Goldschmidt and S. Pauncz studied the catalytic effect of ferrous salts on the oxidizing action of hydrogen dioxide. According to A. Simon and K. Kötschau,



5 to 10 c.c. of a 0.5 per cent. alcoholic soln. of guaiacum resin per 250 c.c. of water, are coloured blue by  $5.6 \times 10^{-6}$  grm. of ferrous iron in presence of hydrogen dioxide in 1 litre of neutral soln., and by  $6.8 \times 10^{-5}$  grm. in a slightly acid soln. The best results are obtained by adding the hydrogen peroxide to the mixture of ferrous salt and guaiacum soln. Light should be excluded, and appreciable amounts of acetic or hydrochloric acid interfere, whereas alkaline soln. do not give the test at all. If "ferrum reductum" is ground up in a mortar, it commences to give the benzidine and guaiacum resin reactions, ferrous hydrogen carbonate being formed by atmospheric moisture and carbon dioxide. By filtration of a suspension of the activated preparation through a membrane filter, an active liquid is obtained, but this gradually loses its activity, the activity towards benzidine and guaiacum resin being a function of the ferrous-ion concentration. By filtering a suspension of ferrum reductum in oxygen-free water saturated with carbon dioxide through a membrane-filter, a liquid results which is active, and retains its activity for weeks, even if light is not excluded, provided that it is kept out of contact with air. The effect of ultra-violet radiation is very slight so long as air is carefully excluded. It is concluded that the activity of natural waters containing iron depends on the presence of ferrous iron, and when this is oxidized the activity disappears. The subject was studied by J. Weiss.

O. Ruff and E. Ascher showed that **fluorine** reacts with ferrous chloride in the cold, and much heat is evolved in the reaction. J. Davy observed that the reaction with **chlorine** is quantitative:  $2\text{FeCl}_2 + \text{Cl}_2 = 2\text{FeCl}_3$ ; and E. Busch observed a similar reaction with ferrous chloride and a soln. of chlorine in methylal. Chlorine also acts as an oxidizing agent in converting ferrous chloride in aq. soln. into ferric chloride (*q.v.*). E. Busch observed that **bromine**, like chlorine, has an oxidizing action on ferrous chloride; and the reaction was studied by V. Rodt and K. Charisius. C. Lenormand found that bromine reacts with ferrous chloride so slowly that the reaction is not completed in a month; when the mixture is heated at  $100^\circ$  in a sealed tube for 24 hrs., a sublimate of ferric bromodichloride is formed. A. W. Francis found that the reaction of bromine on ferrous chloride and sulphate at  $25^\circ$  proceeds at about the same rate. W. D. Bonner and H. Romeyn, and E. Busch observed that **iodine**, like bromine, acts as an oxidizing agent on ferrous chloride in acidic soln. in the presence of phosphoric acid—*vide infra*, ferrous sulphate, and ferric chloride. J. Lifschitz and S. B. Hooghoudt studied the photochemistry of the reaction. G. B. Heisig represented the reaction with **iodine chloride**,  $2\text{FeCl}_2 + 2\text{ICl} = \text{I}_2 + 2\text{FeCl}_3$ . E. C. Franklin found that anhydrous ferrous chloride is insoluble in liquid **hydrogen fluoride**; K. Fredenhagen and G. Cadenbach studied the action of **hydrofluoric acid** on the salt; and K. Fredenhagen added that chlorine is developed. W. Peters observed that the anhydrous salt does not absorb **hydrogen chloride**. V. Meyer, and L. F. Nilson and O. Pettersson observed no chemical change when ferrous chloride is sublimed in an atm. of hydrogen chloride. P. Sabatier observed that the tetrahydrate is soluble in **hydrochloric acid**, but less than is the case with water. H. Lescœur, and P. Sabatier—*vide supra*—showed that when hydrogen chloride is passed into an aq. soln. of ferrous chloride, the hexahydrate or tetrahydrate may be precipitated; and when the soln. is sat. with the gas, the dihydrate is formed. J. Wagner assumed that a *ferrous hydrochloride* is formed in soln. of ferrous chloride in hydrochloric acid, but S. R. Carter and N. J. L. Megson, and T. W. Harrison and F. M. Perkin could not confirm this. W. Preiss studied the influence of ferrous salts on the reduction of **iodides** by chromic acid; and A. K. Goard and E. K. Rideal, W. J. Husa and L. Magid, A. Berthoud and S. V. Allmen, and S. V. Allmen, on the liberation of iodine from iodides and hydrogen dioxide. J. Thomsen represented the oxidation with **hypochlorous acid**:  $2\text{FeCl}_2 \cdot \text{Aq.} + 4\text{HCl} \cdot \text{Aq.} + \text{HOCl} \cdot \text{Aq.} = 2\text{FeCl}_3 \cdot \text{Aq.} + 3\text{HCl} \cdot \text{Aq.} + 54.993 \text{ Cals.}$  J. L. Gay Lussac, and H. Schulze showed that when ferrous chloride is fused with **potassium chlorate**, the products—chlorine and ferric oxide—are similar to those obtained when the chloride is heated in

oxygen. I. M. Kolthoff, O. Collenberg and K. Sandved, and W. Meyerhoffer noted the oxidation of ferrous chloride to ferric chloride by **bromic acid**, or **potassium bromate**.

A. Vogel observed that no iron sulphide is formed when ferrous chloride is heated with **sulphur**. A. W. Ralston and J. A. Wilkinson observed that ferrous chloride is not dissolved by liquid **hydrogen sulphide** at a low temp., or at room temp. The aq. soln. is not reduced by hydrogen sulphide—*vide* ferric chloride. H. de Sénarmont found that when ferrous chloride is heated with **potassium polysulphide** in a sealed tube at 180°, pyrite,  $\text{FeS}_2$ , is formed. According to J. A. Smythe and W. Wardlaw, and W. Wardlaw and F. H. Clews, ferrous chloride in a strongly acid soln. is oxidized to ferric chloride by **sulphur dioxide**:  $4\text{FeCl}_2 + \text{SO}_2 + 4\text{HCl} = 4\text{FeCl}_3 + 2\text{H}_2\text{O} + \text{S}$ , with the possible intermediate formation of thionyl chloride. The proportion of ferric chloride which is formed is nearly independent of the conc. of the ferrous salt, and increases with rise of temp. up to an optimum. If the soln. has less than 145 grms. HCl per litre, no oxidation occurs; and the maximum oxidation in open vessels was 8.8 per cent. of the total iron, in closed vessels 9.5 per cent. Soln. with 10 to 18 per cent. of the total iron as ferric chloride are neither oxidized nor reduced; and soln. with over 18 per cent. are slowly reduced. D. Richter studied the effect of the presence of ferrous chloride on the oxidation of **sodium sulphite** in aq. soln. A. Vogel, and H. Friedrich observed that with cold **sulphuric acid**, ferrous chloride furnishes hydrogen chloride, and ferrous sulphate. J. Thomsen observed that the heat of neutralization of ferrous hydroxide with sulphuric acid is rather greater than it is with hydrochloric acid, so that a little heat is evolved when a dil. soln. of ferrous chloride is treated with dil. sulphuric acid. G. Lunge observed that yellowish-red selenium is formed when a soln. of ferrous chloride is treated with a sulphuric acid soln. of **selenium dioxide**.

A. Guntz found that **lithium nitride** reacts very energetically when it is warmed with ferrous chloride, and if the vigour of the reaction be abated by admixed sodium chloride, iron nitride is formed; A. Smits also observed a vigorous reaction occurs with **magnesium nitride** resulting in the formation of iron nitride which is decomposed at the high temp. of the reaction. According to M. Faraday, H. V. Regnault, A. W. F. Rogstadius, F. Girardet, E. Frémy, W. Peters, F. Ephraim, G. J. Fowler, A. S. Miller, H. N. Warren, and C. Stahlschmidt, at room temp. ferrous chloride readily absorbs **ammonia** to form a voluminous, white mass of the hexammine; at temp. below 350°, the absorption of ammonia is a reversible process, but above that temp. the reaction is not reversible, and a product is formed containing some iron nitride, whilst ammonium chloride, nitrogen, and hydrogen are evolved. C. Stahlschmidt represented the reaction:  $14\text{NH}_3 + 12\text{FeCl}_2 = 4\text{N}_2 + 24\text{HCl} + 6\text{Fe}_2\text{N} + 9\text{H}_2$ . Similar reactions occur when the hexammine is heated above 350°. H. Wolfram said that the reaction at 490° to 530° can be represented by the equation:  $3\text{FeCl}_2 + 8\text{NH}_3 = 3\text{Fe} + \text{N}_2 + 6\text{NH}_4\text{Cl}$ . The metallic iron so formed reacts in part with the nascent nitrogen:  $2\text{Fe} + \text{N} = \text{Fe}_2\text{N}$ ; and in part with ammonia:  $4\text{Fe} + 2\text{NH}_3 = 2\text{Fe}_2\text{N} + 3\text{H}_2$ . According to W. Biltz and E. Rahlfs, ammonia reacts with ferrous chloride to form four amines— $\text{FeCl}_2 \cdot 10\text{NH}_3$ ,  $\text{FeCl}_2 \cdot 6\text{NH}_3$ ,  $\text{FeCl}_2 \cdot 2\text{NH}_3$ , and  $\text{FeCl}_2 \cdot \text{NH}_3$ . Their ranges of existence at different temp. are shown in W. Biltz's diagram, Fig. 561. The amines are formed by absorption of ammonia as just indicated; K. A. Hofmann and co-workers obtained evidence of the formation of an ammine by the action of ammonium chloride on iron at a high temp.; J. Schröder, by the action of ammonia on a soln. of ferrous chloride in pyridine; and E. Weitz and H. Müller, by the action of an ammoniacal

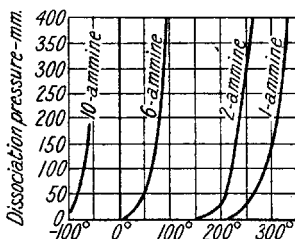
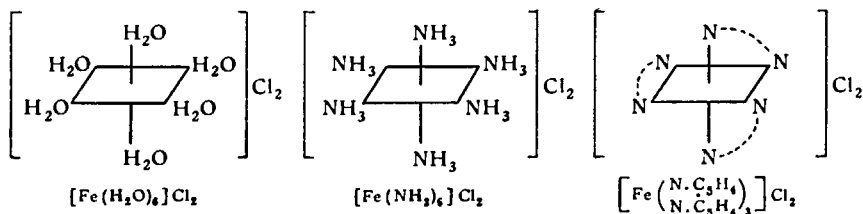


FIG. 561.—The Dissociation Pressures of the Amines of Ferrous Chloride.

soln. of ammonium chloride on a soln. of a ferrous salt. A. S. Miller observed that the ammonia is absorbed by ferrous chloride more readily than is the case with ferric chloride, and much heat is evolved at the same time, and F. Ephraim and co-workers said that these amines are an exception to the rule that by raising the valency of the central atom, the stability of the amines is raised—here the ferrous chloride amines are more stable than those of ferric chloride. W. Biltz and G. F. Hüttig observed that the strength of the union of the  $\text{NH}_3$ -molecule with that of ferrous chloride increases in passing from the hexamine to the diammine to the monammine.

W. Biltz and E. Rahlfs prepared **ferrous decamminochloride**,  $\text{FeCl}_2 \cdot 10\text{NH}_3$ , by the action of liquid ammonia at  $-78.5^\circ$  on anhydrous ferrous chloride. At  $-78.5^\circ$ , the dissociation press.,  $p$ , Fig. 561, is 22 mm.; at  $-70^\circ$ , 49.5 mm.; at  $-65^\circ$ , 77 mm.; at  $-60^\circ$ , 116 mm.; and at  $-55^\circ$ , 173 mm. The heat of formation  $\text{FeCl}_2 \cdot 6\text{NH}_3 + 4\text{NH}_3$  is 29.0 Cals.—i.e. 7.25 Cals. per mol  $\text{NH}_3$ —and this also represents the heat of dissociation. The heat of formation  $(\text{FeCl}_2 \cdot 10\text{NH}_3)_{\text{gas}} = 117$  Cals. When the decammine dissociates, it furnishes **ferrous hexamminochloride**,  $\text{FeCl}_2 \cdot 6\text{NH}_3$ . P. Pfeiffer represented the hexahydrate, the hexamine, and the tridipyridyl-salts, by the formulæ:



F. J. Garrick calculated values for the energy of co-ordination. G. L. Clark discussed the stabilities of the amines. The hexamine was the first ammine to be prepared, as indicated above, by the absorption of ammonia at room temp. W. Biltz and G. F. Hüttig preferred to saturate the anhydrous chloride at a low temp., and evaporate the excess of ammonia at room temp. E. Weitz and H. Müller obtained it as indicated above, and W. Hieber and G. Bader, by the action of ammonia on iron dichlorotetracarbonyl,  $\text{Fe}(\text{CO})_4\text{Cl}_2$ . According to W. Biltz, and A. Werner, the ammonia in the hexamine is part of the cation  $[\text{Fe}(\text{NH}_3)_6]\text{Cl}_2$ , and in the molecule, the  $\text{Fe}^{++}$ -atom is surrounded by an octahedral ring of molecules of ammonia. G. F. Hüttig added that six is the maximum number of ammonia molecules which can be arranged about the central iron atom. W. Biltz and E. Birk also discussed the packing density of the ammonia molecules. All observers agree that the hexamine prepared in the dry way is a voluminous, white or grey powder; and W. Biltz added that it occupies three times the vol. of the original ferrous chloride. E. Weitz and H. Müller added that the white colour is due to the fine state of subdivision of the hexamine, for when prepared in crystals by a wet process, the colour is pale green, and soln. containing the ion  $[\text{Fe}(\text{NH}_3)_6]^{++}$  have the same colour. According to W. Biltz, the crystals are cubic, and isomorphous with other hexamines of the iron-family. The X-radiogram shows that the space-lattice has the parameter  $a=10.19$  Å. The chlorine atoms are related to the iron atoms like the fluorine atoms are related to the calcium atoms in fluorspar. The centre of a  $\text{NH}_3$ -molecule is about  $\frac{1}{4}a$  from the middle of a metal atom which is surrounded by an octahedral ring of the ammonia molecules. G. B. Naess and O. Hassel studied the sphere of action of the anion. W. Biltz and E. Birk found the sp. gr. to be 1.428 at  $25^\circ/4^\circ$ . F. Girardet found the dissociation press.,  $p$  mm., to be:

	$0^\circ$	$14^\circ$	$50^\circ$	$70^\circ$	$90^\circ$	$100^\circ$	$115^\circ$
$p$ . . . . .	0	5	11	93	270	425	743

and F. Ephraim (Fig. 561):

	64.5°	75°	85.5°	100.5°	105.7°	108.8°	115°
<i>p</i> . . . . .	82	130	203	375	490	547	715

F. Müller gave  $-18^{\circ}$  to  $95^{\circ}$  for the dissociation temp. G. Beck gave 317 cal. for the heat of formation of the hexammine; and W. Hieber and E. Levy studied the subject. W. Biltz and co-workers, and F. Ephraim calculated for the heat of formation  $(\text{FeCl}_2, 6\text{NH}_{3\text{gas}}) = 87.96$  Cals.—or 14.66 Cals. per mol.  $\text{NH}_3$ —and for  $(\text{FeCl}_2, 2\text{NH}_3, 4\text{NH}_{3\text{gas}}) = 49.0$  Cals.—or 12.25 Cals. per mol.  $\text{NH}_3$ . The maximum work or affinity of the reaction  $(\text{FeCl}_2, 6\text{NH}_3)$  at  $27^{\circ}$ , and atm. press., is 31.08 Cals.—or 5.18 Cals. per mol. of  $\text{NH}_3$ . F. J. Garrick calculated the energy of co-ordination. M. Faraday, A. S. Miller, G. J. Fowler, and H. Wolfram observed that when the white hexammine is exposed to air, it becomes yellow or green, brown, and finally black. The hexammine prepared in a wet way was found by E. Weitz and H. Müller to decompose in a similar manner on exposure to air. A. W. F. Rogstadius observed that when heated out of contact with air, the hexammine sinters and then fuses to a dark brown mass with the composition  $3\text{FeCl}_2, 2\text{NH}_3$ . G. B. Naess and O. Hassel observed that the hexammine forms  $[\text{Fe}(\text{NH}_3)_6](\text{BF}_4)_2$ , and  $[\text{Fe}(\text{NH}_3)_6](\text{SO}_3\text{F})_2$ .

F. Girardet, H. Wolfram, and W. Biltz and G. F. Hüttig observed that when the hexammine is heated, it passes, without the formation of an intermediate compound, into **ferrous diamminochloride**,  $\text{FeCl}_2, 2\text{NH}_3$ . A. S. Miller recommended heating the hexammine to  $100^{\circ}$  in a current of hydrogen. W. Biltz said that the ammonia of the diammine is associated with the anion, and that the co-ordination number is 4. F. Girardet gave for the dissociation press., *p* mm.:

	96°	135°	160°	205°	255°	270°	272°
<i>p</i> . . . . .	1	5	13	62	378	601	727

but W. Biltz and G. F. Hüttig said that these values are too high, and they gave  $p = 121$  mm. at  $230^{\circ}$ , and 555 mm. at  $277^{\circ}$ . F. Müller gave  $240^{\circ}$  to  $270^{\circ}$ . According to W. Biltz and G. F. Hüttig, the heat of formation  $(\text{FeCl}_2, 2\text{NH}_{3\text{gas}}) = 38.96$  Cals. or 19.48 Cals. per mol. of  $\text{NH}_3$ ; and  $(\text{FeCl}_2, \text{NH}_3, \text{NH}_{3\text{gas}}) = 18.20$  Cals. The maximum work or affinity of the reaction  $(\text{FeCl}_2, 2\text{NH}_3)$  at  $27^{\circ}$ , and atm. press., is 19.5 Cals.—or 9.75 Cals. per mol. W. Hieber and E. Levy studied the energy of formation. According to H. Wolfram, the diammine passes into **ferrous monamminochloride**,  $\text{FeCl}_2, \text{NH}_3$ , at  $260^{\circ}$ , and W. Biltz and G. F. Hüttig suggested  $276.7^{\circ}$ . W. Biltz said that the ammonia of the monammine is associated with the anion. The dissociation press., *p* mm., was found by W. Biltz and co-workers to be 5.8, 10.9, and 54.4 mm. respectively at  $214.5^{\circ}$ ,  $230^{\circ}$ , and  $277^{\circ}$ . H. Wolfram said that the monammine loses 0.9 mol. of ammonia at  $320^{\circ}$ . F. Müller said over  $300^{\circ}$ . W. Biltz and co-workers gave for the heat of formation  $(\text{FeCl}_2, \text{NH}_3) = 20.76$  Cals.; and for the maximum work or affinity, at  $27^{\circ}$ , and atm. press., 11.06 Cals. F. Ephraim and R. Linn, and W. Biltz and G. F. Hüttig also found that ferrous chloride forms **ferrous hexamethylaminochloride**,  $\text{FeCl}_2, 6(\text{CH}_3, \text{NH}_2)$ ; and grey **ferrous dimethylaminochloride**,  $\text{FeCl}_2, 2(\text{CH}_3, \text{NH}_2)$ , by the action of **methylamine**, in place of ammonia or ferrous chloride. For the action of **hydroxylamine**, *vide* ferric chloride.

H. Goldschmidt and K. L. Syngros found that when an excess of **hydroxylamine hydrochloride** and sodium carbonate is added to a soln. of ferrous chloride, the soln. becomes dark red, due, it is thought, to the formation of **ferrous hydroxylaminochloride**,  $[\text{Fe}(\text{NH}_2\text{OH})_2]\text{Cl}_2$ . O. von Mayer, and H. Franzen and O. von Mayer added **hydrazine hydrate** to a 15 per cent. alcoholic soln. of ferrous chloride, and obtained a brown precipitate; when the mixture is warmed, gas is given off and the yellow, pulverulent **ferrous hydrazinochloride**,  $\text{FeCl}_2, 2\text{N}_2\text{H}_4$ , is formed. The magnetic properties were examined by D. M. Bose, and P. Ray and H. Bhar. The action of **nitric oxide** on ferrous salts has been previously discussed—8. 49, 35—by H. I. Schlesinger and H. B. van Valkenburgh. W. Manchot and C. Zechentmayer, W. Manchot and F. Huttner, V. N. Morris, T. Graham, J. Gay, V. Thomas,

and I. Bellucci. The compounds  $\text{FeCl}_2 \cdot \text{NO} \cdot 2\text{H}_2\text{O}$ , and  $\text{FeCl}_2 \cdot \text{NO}$  first described by V. Thomas were afterwards shown to be wrong. According to V. Thomas, if nitric oxide, free from nitrous oxide, be passed over anhydrous ferrous chloride, a little nitric oxide is absorbed, and the product acquires a red colour—the dark colour observed by T. Graham was due to the presence of some nitrous oxide—if the temp. be in the vicinity of  $300^\circ$ , the product approximates  $10\text{FeCl}_2 \cdot \text{NO}$  to  $12\text{FeCl}_2 \cdot \text{NO}$ . When ferric chloride is reduced by distillation in an atm. of nitric oxide, **ferrous heminitrosylchloride**,  $2\text{FeCl}_2 \cdot \text{NO}$ , is formed:  $2\text{FeCl}_3 + 3\text{NO} = 2\text{NOCl} + 2\text{FeCl}_2 \cdot \text{NO}$ ; if the ferric chloride be heated in a rapid current of nitric oxide, the reaction is symbolized  $\text{FeCl}_3 + \text{NO} = \text{FeCl}_2 + \text{NOCl}$ . The heminitrosylchloride is a yellowish-brown powder; decomposed by water; stable in dry air, but decomposed by moist air. When heated in air, it forms ferric oxide, but in nitrogen, it gives off nitric oxide and yields ferrous chloride. H. Müller observed that if an ammoniacal soln. of an ammonium salt and ferrous chloride be treated, in the cold, with nitric oxide, there is formed **ferrous nitrosyl-pentamminochloride**,  $[\text{Fe}(\text{NO})(\text{NH}_3)_5]\text{Cl}_2$ . The black, octahedral crystals decompose on exposure to air. V. Thomas observed that anhydrous ferrous chloride, at room temp., absorbs dry **nitrous oxide** without oxidation. The absorption is faster than is the case with nitric oxide. The compound approximates **ferrous tetritanitroxylchloride**,  $4\text{FeCl}_2 \cdot \text{NO}_2$ . If water be present, more nitrous oxide is absorbed, and some chlorine is evolved. The tetranitroxylchloride is black, and it is stable in dry air or in vacuo; it is decomposed by water with the partial oxidation of the iron. The red, aq. soln. forms a black precipitate when treated with alkali. H. Gall and H. Mengdehl found that when **nitrosyl chloride** is passed over ferrous chloride, the mass becomes warm, swells up, and nitric oxide is evolved. There is a reaction  $\text{FeCl}_2 + \text{NOCl} = \text{FeCl}_3 \cdot \text{NO}$ ; then follows the formation of  $\text{FeCl}_3 \cdot \text{NOCl}$ . At a low temp., ferrous chloride reacts with liquid nitrosyl chloride at  $-20^\circ$  to form crystals of  $\text{FeCl}_3 \cdot \text{NOCl}$ . A. Joly and E. Leidié, and P. Schwarzkopf found that when a soln. of ferrous chloride is treated with **alkali nitrite** until it reacts alkaline, a brown gelatinous precipitate is formed; and J. Thiele observed that on adding a conc. soln. of sodium nitrite to a hydrochloric acid soln. of ferrous chloride, a regular stream of nitric oxide is evolved:  $\text{FeCl}_2 + \text{NaNO}_2 + 2\text{HCl} = \text{FeCl}_3 + \text{NaCl} + \text{H}_2\text{O} + \text{NO}$ . R. Thomas and E. T. Williams observed that the presence of a little sodium nitrite catalyzes the slow oxidation of a soln. of ferrous chloride by air. Ferrous chloride is oxidized to ferric chloride (*q.v.*) by **nitric acid**. L. H. Milligan and G. R. Gillette, and R. Hac and V. Netuka studied the reduction of nitric acid by ferrous chloride using molybdic acid as catalyst. A. Quartaroli showed that if nitrous acid be removed, nitric acid does not act as an oxidizing agent, so that in presence of carbamide, an amino-acid, or an amide, nitric acid does not oxidize ferrous salts because these agents destroy the nitrous acid.

A. Granger observed that **phosphorus** vapour at dull redness converts ferrous chloride into iron phosphide,  $\text{Fe}_2\text{P}_3$ . H. Rose observed that ferrous chloride reacts in the cold with **phosphine** forming hydrogen chloride and iron phosphide. W. Peters said that no phosphine is absorbed by anhydrous ferrous chloride. A. W. Cronander observed that **phosphorus pentachloride** acts on warm ferrous chloride forming phosphorus trichloride and  $\text{FeCl}_3 \cdot \text{PCl}_5$ . H. P. Cady and R. Taft said that ferrous chloride is perceptibly soluble in **phosphoryl chloride**. D. Richter studied the catalytic oxidation of ferrous ions on **hypophosphorous acid**. E. Fischer observed that when a hydrochloric acid soln. of ferrous chloride is heated with **arsenic acid**, volatile arsenic trichloride is formed. H. Sommerlad said that anhydrous ferrous chloride reacts when it is heated with **antimony trisulphide** forming antimony trichloride. A. Béchamp and C. St. Pierre found that **antimony trichloride** is not reduced by a boiling soln. of ferrous chloride; and R. F. Weinland and co-workers obtained a complex salt by the action of **bismuth chloride** on a soln. of ferrous chloride.

N. Schiloff and L. Lepin, and N. Schiloff studied the adsorption of ferrous

chloride from aq. soln. by **carbon**. F. W. O. de Coninck observed that unlike a soln. of ferric chloride, a soln. of ferrous chloride suffers no change when it is filtered through animal charcoal. W. Peters found that anhydrous ferrous chloride absorbs no **carbon monoxide**. By the action of dry chlorine on **iron carbonyl**,  $\text{Fe}(\text{CO})_5$ , in petroleum ether at  $-20^\circ$ , W. Hieber and co-workers prepared **ferrous tetracarbonyl chloride**,  $\text{Fe}(\text{CO})_4\text{Cl}_2$ ; by the action of dry chlorine on mercuric iron carbonyl,  $\text{Fe}(\text{CO})_4\text{Hg}$ , H. Hock and H. Stuhlmann obtained the same salt. It gives off carbon monoxide slowly if the temp. exceeds  $10^\circ$ , or the press. is below 750 mm. The soln. in nitrobenzene is decomposed on exposure to light; and it is decomposed by water into ferrous chloride and carbon monoxide; with ammonia it forms ferrous hexamminochloride; and with pyridine it forms ferrous pyridinochloride. If the temp. at which the chlorine acts on the pentacarbonyl is very low, **ferrous pentacarbonyl chloride**,  $\text{Fe}(\text{CO})_5\text{Cl}_2$ , is formed. M. Hannik studied the oxidation of ferrous salts by **potassium ferricyanide**.

W. Manchot and J. Haas said that an aq. soln. of ferrous chloride does not react with **ethylene**. J. Kachler showed that when an ethereal soln. of hydrated ferrous chloride is heated in a sealed tube, colourless, acicular crystals of **ferrous ethylenechloride**,  $\text{FeCl}_2 \cdot \text{C}_2\text{H}_4 \cdot 2\text{H}_2\text{O}$ , soluble in water, are formed—*vide infra*, ether. V. Thomas observed that ferrous chloride is soluble in **ethylene chloride**, and in **ethylene bromide**—the soln. absorb nitric oxide. W. Peters said that anhydrous ferrous chloride does not absorb ethylene or **acetylene**. V. Thomas observed that ferrous chloride is slightly soluble in **benzene**. Ferrous chloride is soluble in **methyl alcohol**. A. Benrath observed that when a soln. of ferric chloride in methyl alcohol is illuminated, ferrous chloride is formed and the soln. deposits colourless crystals of **ferrous methylalcoholochloride**,  $\text{FeCl}_2 \cdot 4\text{CH}_3\text{OH}$ . The soln. in methyl alcohol was found by K. A. Hofmann and G. Bugge to be rapidly oxidized by air; V. Kohlschütter and P. Sazanoff, that it absorbs nitric oxide; K. A. Hofmann and G. Bugge, that it precipitates ferrous cyanide when treated with hydrocyanic acid; and with ethyl carbylamine, it gives crystals of a ferric salt,  $\text{Fe}_2\text{Cl}_4\text{O} \cdot 5\text{C}_3\text{H}_5\text{N}$ ; and L. Levi-Bianchini observed that the chloride is decomposed at the critical temp. of the soln. C. F. Wenzel, M. Hamers, and F. Jahn observed that anhydrous ferrous chloride is soluble in conc. **ethyl alcohol**. R. Boyle noted that the tetrahydrate is soluble in alcohol. T. Graham noted that the anhydrous chloride adsorbs the vapour of ethyl alcohol as well as steam. G. Pellini and D. Meneghini observed that the yellowish-green soln. becomes paler when it is cooled. When the soln. is exposed to sunlight, L. E. Jonas said that ferric hydroxide is precipitated. C. Cattaneo found that the sp. electrical conductivities referred to mercury at  $0^\circ$ , of soln. with 0.0823, 0.0088, and 0.00087 eq. of the salt per litre, at  $18^\circ$ , are  $27.4 \times 10^9$ ,  $5.67 \times 10^9$ , and  $1.02 \times 10^9$  respectively, and the temp. coeff. 0.014, 0.012, and 0.015 respectively. The sp. conductivity of the alcohol alone was  $0.221 \times 10^9$  at  $18^\circ$ . M. Faraday found that the soln. is paramagnetic; C. Matteucci examined the magnetic properties of non-homogeneous mixtures of the soln. with olive oil. G. Pellini and D. Meneghini said that when hydrogen is passed through the soln. it remains clear, but with oxygen it becomes turbid. The oxidation of the soln. by air was studied by K. A. Hofmann and G. Bugge, P. Nicolardot, and A. G. Doroschewsky and A. J. Bardt. According to V. Thomas, the evaporation of the soln. furnishes crystals of ferrous chloride associated with alcohol of crystallization. K. Seubert and A. Dorrer found that with an alcoholic soln. of iodide, a deep brown liquid is formed containing  $\text{FeCl}_2\text{I}$ . F. Huttner, and W. Manchot and F. Huttner observed that the soln. absorbs nitric oxide. W. Manchot and J. Haas observed that neither carbon monoxide nor ethylene unites with the salt in alcoholic soln. F. Saenger observed that an alcoholic soln. of sodium alcoholate forms a black substance with anhydrous ferrous chloride—possibly ferrous alcoholate.

F. Jahn said that ferrous chloride is insoluble in **ether**; and H. E. Williams, that the tetrahydrate is only sparingly soluble in ether. A. F. Gehlen obtained a

precipitate of a ferrous salt when the ethereal soln. is exposed to light. C. Cattaneo gave 0.00125 for the sp. electrical conductivity of 0.001*N*-FeCl<sub>2</sub> at 18°, and —0.020 for the temp. coeff. V. Thomas obtained red, prismatic crystals when the ethereal soln. is evaporated. W. Manchot and J. Haas could not prepare a compound of ether and ferrous chloride directly, but by warming an ethereal soln. of ferric chloride, best with the addition of phosphorus at 140° to 150°, a complex salt was formed, and it is probably the complex which J. Kachler reported as ferrous ethylenechloride. V. Thomas noted the absorption of nitric oxide by the ethereal soln. K. A. Hofmann and G. Bugge obtained analogous results with ethyl carbylamine to those obtained with the soln. in methyl alcohol. When the aq. soln. of ferrous chloride is treated with ether, F. Jahn observed that the ethereal layer is almost free from iron. H. Wieland and F. Chrometzka studied the catalytic decomposition of **ethyl peroxide** by ferrous salts. W. Eidmann, W. H. Krug and K. P. McElroy, P. Schulz, and A. Naumann and P. Schulz found that ferrous chloride is soluble in **acetone** forming a yellow soln. A brown precipitate is simultaneously formed—probably a ferric oxychloride. P. Schulz said that acetone oxidizes a soln. of ferrous chloride to ferric chloride. F. Huttner, and W. Manchot and F. Huttner observed that the acetone soln. absorbs nitric oxide. V. Thomas observed that ferrous chloride is slightly soluble in glacial **acetic acid**, and the soln. absorbs nitric oxide. J. Rill, and A. Naumann and J. Rill found that ferrous chloride is sparingly soluble in **methyl acetate**. S. Hakomori studied the action of **oxalic, citric, malic, and succinic acids**. E. Linckh, F. Huttner, W. Manchot and F. Huttner, E. Alexander, and A. Naumann and E. Alexander observed that the soln. in **ethyl acetate** is 0.04*M*, and it absorbs nitric oxide; E. Linckh, and F. Huttner and E. Linckh, that the soln. in **ethyl malonate** is 0.01*M*, and it absorbs nitric oxide; F. Huttner, and W. Manchot and F. Huttner, that the soln. in **ethyl benzoate** is 0.0667*M*, and it absorbs nitric oxide; and W. Eidmann observed that the salt is insoluble in **methylal**. V. Thomas found that, in the cold, **phenol** does not dissolve ferrous chloride, and when heated, there is a reaction with the evolution of heat and the formation of a black product. B. Köhnlein observed no reaction with **propyl chloride**. E. Shpolsky examined the retarding effect of ferrous chloride on the photochemical decompositions of Eder's soln.

A. Schier, and A. Naumann and A. Schier found that ferrous chloride readily dissolves in **acetonitrile** forming a colourless soln.; and A. Naumann, and J. Kämmerer, that it forms a yellow soln. with **benzonitrile**. W. Hieber and co-workers, and R. E. Breuil prepared a complex with **ethylenediamine**, [Fe en<sub>3</sub>]Cl<sub>2</sub>. J. C. Duff and E. J. Bills observed that with **hexamethylenetetramine**, pale green, microcrystalline plates of **ferrous hexamethylenetetraminohydrochloride**, FeCl<sub>2</sub>·2C<sub>6</sub>H<sub>12</sub>N<sub>4</sub>·9H<sub>2</sub>O, are formed. According to J. Schröder, and A. Naumann and J. Schröder, when anhydrous ferrous chloride is treated with **pyridine**, a part forms a greenish-yellow soln., and a part forms a complex ferrous pyridinohydrochloride. F. Reitzenstein found a feebly acidified soln. of ferrous chloride gives a dark green colour with an excess of pyridine. A. Werner and W. Schmutjloff measured the raising of the b.p. of pyridine by the ferrous salt, but J. Schröder showed that the b.p. is lowered, not raised. E. Linckh said that the most conc. soln. is 0.1*M*. N. Costachescu and G. Spacu observed that the soln. becomes reddened by oxidation in air. J. Schröder found that a fresh soln. is not changed by water, but an aged soln. deposits ferric hydroxide. Chlorine, bromine, and iodine act as oxidizing agents; soluble chlorides, bromides, and iodides have no action; the halide acids, and sulphur dioxide have no perceptible effect; dry hydrogen sulphide has at first no perceptible action, but traces of ferrous sulphide are precipitated after a prolonged action; ammonia gives a reddish-brown substance which is rapidly darkened on exposure to air; F. Huttner, and E. Linckh found that nitric oxide is absorbed by the soln.; and J. Schröder, that with ammonium thiocyanate, ammonium chloride is precipitated; metals have no action; and silver sulphate precipitates ferrous sulphate. N. Costachescu and

G. Spacu, and R. Weinland and co-workers prepared **ferrous tetrapyridinechloride**,  $\text{FeCl}_2 \cdot 4\text{C}_5\text{H}_5\text{N}$ , by the action of pyridine on anhydrous ferrous chloride in the cold; and W. Hieber and co-workers, by the action of 4 or more mols of pyridine on a mol of  $\text{Fe}(\text{CO})_4\text{Cl}_2$ . It is not yet settled whether the co-ordination formula is  $[\text{Fe}(\text{C}_5\text{H}_5\text{N})_4\text{Cl}_2]$  or  $[\text{Fe}(\text{C}_5\text{H}_5\text{N})_4]\text{Cl}_2$ . The canary-yellow, crystalline salt is stable in an atm. of pyridine, but it is slowly oxidized by dry air; it is decomposed by water. W. Hieber and E. Levy studied the heat of formation; and O. Stelling, the X-ray spectrum. R. Weinland and co-workers found that when the complex is treated with methyl or ethyl alcohol, it loses 2 mols. of pyridine forming **ferrous dipyridinechloride**,  $\text{FeCl}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$ ; and W. Hieber and G. Bader obtained the same product by the action of 2 mols of pyridine on one mol of  $\text{Fe}(\text{CO})_4\text{Cl}_2$ . F. Reitzenstein, and P. Pfeiffer reported  $\text{FeCl}_2 \cdot 3\text{C}_5\text{H}_5\text{N} \cdot \text{H}_2\text{O}$ , which N. Costachescu and G. Spacu consider to be the impure tetrapyridinechloride. W. Hieber and E. Levy studied the heat of formation, and O. Stelling the X-ray spectrum. F. L. Hahn and H. Wolf reported a compound with  $\alpha$ -**acetaminopyridine**, namely **ferrous  $\alpha$ -acetaminopyridinechloride**,  $[\text{Fe}(\text{C}_7\text{H}_8\text{N}_2\text{O})_2]\text{Cl}_2$ ; J. L. C. Schröder van der Kolk, and A. R. Leeds, a complex with **aniline**, namely **ferrous dianilinechloride**,  $\text{FeCl}_2 \cdot 2\text{C}_6\text{H}_5\text{NH}_2$ ; F. Blau, and T. M. Lowry, a complex with  $\alpha, \alpha'$ -**dipyridyl**, namely **ferrous  $\alpha, \alpha'$ -dipyridylchloride**,  $[\text{Fe}(\text{C}_{10}\text{H}_8\text{N}_2)_2]\text{Cl}_2$ ; and F. Blau, a compound with  $\alpha$ -**phenantrolin**, namely **ferrous  $\alpha$ -phenantrolinchloride**,  $[\text{Fe}(\text{C}_{12}\text{H}_8\text{N}_2)_3]\text{Cl}_2 \cdot n\text{H}_2\text{O}$ . K. Kimura and H. Sueda prepared a complex with **dimethylglyoxime**; P. Pfeiffer and F. Tappermann, compounds with **tridiphenyl-** and **triphenanthrolin**; W. Manchot and H. Gall studied the action of ferrous chloride on **ethylene mercaptan**; K. Lehmstedt, on secondary **nitrosamines**; J. H. Long, on the inversion of **cane sugar**; and E. Borsbach, on **quinoline**. S. Swann found that iron salts inhibit the electrolytic reduction of **benzophenone**. R. Chenevix observed that **tincture of glass** reacts when the soln. of ferrous chloride has been exposed to air for some time. J. Dunin-Borkowsky observed the coagulation of **blood** by soln. of ferrous chloride; and W. Pauli studied the action of the salt on soln. of **albumin**.

G. Gore observed that precipitated and calcined **silica** adsorbs no ferrous chloride from a 10 per cent. aq. soln., although the temp. rises about  $0.33^\circ$  if 6.5 grms. of silica be added to 50 c.c. of the soln. A. Gorgeu observed that when a moist current of hydrogen is passed over silica and molten chloride, ferrous oxide, and an oxy-chloride are the chief products, and a neutral ferrous silicate,  $\text{Fe}_2\text{SiO}_4$ , fayalite is also formed; **ferrous silicate** and ferrous chloride form a little chlorosilicate; and when ferrous chloride is melted with **clay**, ferrous silicate and aluminate are formed. The Glauber's iron tree observed by J. R. Glauber in 1648, is formed when a crystal of hydrated ferrous chloride is placed in a soln. of **water-glass**. It was studied by G. J. Mulder. C. Friedel and J. Guérin observed no complex is formed when ferrous chloride is treated with **titanium tetrachloride**—cold or warm. For the action of **titanous chloride**, *vide* 7. 41, 12. According to J. Hoffmann, green, iridescent crystals of a complex are formed with ferrous chloride and **boron trichloride**—namely **ferrous borochloride**,  $3\text{FeCl}_2 \cdot \text{BCl}_3$ —when ferroboration is heated in chlorine.

J. Michajlenko and P. Muschinsky observed that upwards of  $40^\circ$ , **magnesium** powder reacts with tetrahydrated ferrous chloride with the evolution of hydrogen; the reaction was discussed by H. N. Warren. J. A. Poumarède found that with **zinc** vapour, ferrous chloride mixed with a little carbon forms dendritic crystals of iron; and H. N. Warren observed that molten zinc acts on a mixture of sodium and ferrous chlorides in accord with  $\text{Zn} + \text{FeCl}_2 = \text{ZnCl}_2 + \text{Fe}$ .

M. Canac found that if the surface of **aluminium** is rubbed with a hydrochloric acid soln. of ferrous chloride, it becomes lustrous. J. Brown observed that **iron** is attacked by molten ferrous chloride; and C. F. Schönbein, that iron in contact with a soln. of ferrous chloride rusts more rapidly than it does in contact with water. F. Bergius also noted that at an elevated temp., water attacks iron forming



ferrous oxide more slowly than is the case with a soln. of ferrous chloride.

A. Ferrari and M. Carugati found that molten ferrous chloride attacks **platinum**.

H. Meyer discussed the extraction of **cupric oxide** from roasted ores by an aq. soln. of ferrous chloride. T. S. Hunt represented the reaction:  $3\text{CuO} + 2\text{FeCl}_2 = 2\text{CuCl} + \text{CuCl}_2 + \text{Fe}_2\text{O}_3$ . The reaction is retarded by the sparing solubility of the cuprous chloride. The solubility of this salt is raised by adding some sodium chloride and warming the mixture. Actually the iron is deposited as hydrated ferric oxide and possibly a basic ferric chloride. If a large excess of cupric oxide be present, some basic cupric chloride is formed. With **cuprous oxide**, hydrated ferric oxide is formed, and there is a partial reduction of the oxide to metal,  $3\text{Cu}_2\text{O} + 2\text{FeCl}_2 = 4\text{CuCl} + 2\text{Cu} + \text{Fe}_2\text{O}_3$ . If sodium chloride be also present, the cuprous chloride passes into soln. W. Kwasnik represented the reaction with **barium dioxide**:  $4\text{FeCl}_2 + 4\text{BaO}_2 + 6\text{H}_2\text{O} = 4\text{Fe}(\text{OH})_3 + 4\text{BaCl}_2 + \text{O}_2$ . H. Rose, and A. Mailhe observed that when freshly-prepared, moist **mercuric oxide** is added to a soln. of ferrous chloride, a black powder is formed which then becomes a brown mixture of mercurous chloride and ferric oxychloride—the soln. contains mercuric chloride. If only a small proportion of mercuric oxide is added to the soln., white mercurous chloride is precipitated, and the ferric salt remains in soln. H. Pélabon and M. Delwaulle obtained ferric oxide and mercurous chloride as products of the reaction. C. F. Schönbein observed that when **lead dioxide** is added to the soln. of ferrous chloride, a ferric salt and lead chloride are formed. H. Schulze observed that when ferrous chloride is heated with **molybdenum trioxide**, in a stream of carbon dioxide, the reaction can be represented:  $\text{FeCl}_2 + 2\text{MoO}_3 = \text{FeMoO}_4 + \text{MoO}_2\text{Cl}_2$ ; and similarly with **tungsten trioxide**. C. Zengelis found that ferrous chloride does not reduce hydrochloric acid soln. of **molybdates** even when warmed. A. Geuther and E. Forsberg found that when ferrous chloride is melted with **sodium tungstate**, ferrous tungstate and sodium chloride are formed. According to C. Marchal and J. Wiernik, when freshly precipitated **manganese dioxide** is added to a neutral soln. of ferrous chloride, the iron is oxidized quantitatively to a ferric salt. M. Kuhara observed that whilst a soln. of ferrous chloride or a suspension of ferrous hydroxide in water is not changed by boiling, yet, if air be excluded, **ferrous hydroxide** suspended in a boiling, conc. soln. of ferrous chloride, slowly forms magnetite:  $\text{FeCl}_2 + 2\text{Fe}(\text{OH})_2 = \text{Fe}_3\text{O}_4 + 2\text{HCl} + \text{H}_2$ ; with a 15 per cent. soln. of ferrous chloride, hæmatite is formed. Similar results are obtained if a little alkali, powdered calcite, or siderite be added to a soln. of ferrous chloride, and the mixture boiled. When **ferric oxide** is boiled for 5 hrs. with a 20 per cent. soln. of ferrous chloride, magnetite is formed. M. Curie and J. Saddy found that the luminescence of zinc sulphide is diminished by ferrous chloride. E. Schürmann observed that **lead sulphide** is not attacked by a soln. of ferrous chloride.

I. I. Krasikoff and I. T. Ivanoff discussed the solubility of ferrous chloride in soln. of various **metal chlorides**. The aq. soln. of ferrous chloride was found by E. Petersen to become turbid when treated with **potassium fluoride**. The complex salts with the chlorides of ammonium, lithium, sodium, potassium, rubidium, cæsium, magnesium, and cadmium are discussed below. According to T. S. Hunt, **cuprous chloride** dissolves in a soln. of ferrous chloride, and R. Kremann and F. Noss added that the solubility of the cuprous salt increases with the conc. of the ferrous chloride, and the solubility of ferrous chloride in water is likewise raised by the presence of cuprous chloride. When the conc. soln. is diluted, cuprous chloride is precipitated. A complex salt is considered to be formed though it has not been isolated. R. Rosendahl studied the reaction. D. Roberts and F. G. Soper studied the reduction of **silver nitrate** by ferrous sulphate soln.:  $\text{Ag}^+ + \text{Fe}^{++} \rightarrow \text{Fe}^{+++} + \text{Ag}$ . Ferrous chloride reduces a soln. of **gold chloride**. P. A. von Bonsdorff noticed the precipitation of a complex salt when soln. of ferrous chloride and **mercuric chloride** are mixed—*vide infra*. J. Lifschitz and S. B. Hooghoudt studied the photochemistry of the reaction. According to C. Winther, a soln. of mercuric

chloride is reduced by ferrous chloride when exposed to light, and mercurous chloride is formed:  $\text{HgCl}_2 + \text{FeCl}_2 = \text{FeCl}_3 + \text{HgCl}$ . When the conc. of the mercuric chloride is constant and relatively small, the rate is nearly independent of the conc. of the ferrous salt. For a given conc. of the latter, the rate increases at first with the amount of mercuric chloride and then diminishes. The maximum is attained when the two salts are present in equimolar quantities. In the case of soln. containing small quantities of mercuric relatively to ferrous chloride, the sensitiveness increases with the dilution, but this is not the case for soln. containing equimolar quantities. Such soln. do not vary to the same extent when the conc. is changed, and the maximum sensitiveness is shown by soln. containing the two salts in 3*M*-conc. The presence or absence of oxygen is without appreciable influence on the equimolar soln., but oxygen reduces the quantity of mercurous chloride obtained when a large excess of ferrous chloride is present. The most active light rays are those of wavelength less than  $265\mu$ . This is shown by comparative experiments in quartz, uviol glass, and ordinary glass vessels. A. Béchamp and C. St. Pierre found that **stannous chloride** is not reduced by a boiling soln. of ferrous chloride, whilst with **stannic chloride**, J. Biron obtained a complex salt—*vide infra*. According to N. Bouman, by the addition of a soln. of stannous chloride, the potential of iron in a soln. of ferrous chloride becomes less negative, so that it is then less electro-negative than tin; consequently, it is no longer in the state to precipitate tin from its soln. At the same time, it is shown that reduced iron will precipitate tin from its soln. if boiled with a slightly acidic soln. of stannous chloride. The subject was discussed by I. M. Kolthoff, and F. G. Soper. A. Béchamp observed that a strongly basic soln. of **ferric chloride** gives a precipitate when treated with ferrous chloride, and the precipitate is dissolved when water is added. A. Béchamp and C. St. Pierre found that a soln. of **platinous chloride** is not reduced by a soln. of ferrous chloride. L. F. Nilson observed the formation of complex salts; and P. A. von Bonsdorff found that a complex chloroplatinate is formed when a soln. of **platinic chloride** and ferrous chloride is evaporated.

H. Meyer found that a cold, neutral soln. of ferrous chloride, in the absence of air, attacks **copper carbonate** with the evolution of carbon dioxide, and the formation of hydrated ferric oxide:  $2\text{FeCl}_2 + 3\text{CuCO}_3 = 3\text{CO}_2 + \text{Fe}_2\text{O}_3 + \text{CuCl}_2 + 2\text{CuCl}$ , and if a sufficient excess of ferrous chloride is present, the cuprous chloride remains in soln. H. Meyer, and J. A. Buchner found that with **calcium carbonate**, as calcite, no change occurs on standing many days in a soln. of ferrous chloride; but a boiling soln. attacks the crystal superficially; the finely-powdered carbonate is more rapidly attacked. J. Sprenger also studied the reaction. E. M. Walton found that when crystals of tetrahydrated ferrous chloride and enneahydrated **ferric nitrate** are triturated together, the mixture becomes liquid.

**Complex salts of ferrous chloride.**—J. J. Berzelius and W. Hisinger observed that if iron filings be boiled with a sat. soln. of ammonium chloride in a closed vessel, ammonia and hydrogen are evolved, and a soln. is formed, which, on crystallization furnishes bluish-green crystals of **ammonium ferrous tetrachloride**, or *ammonium tetrachloroferrite*, which, in accord with C. A. Winkler's, and A. Chassevant's analyses, are probably  $2\text{NH}_4\text{Cl} \cdot \text{FeCl}_2$ , or  $(\text{NH}_4)_2\text{FeCl}_4$ . A. Vogel, and C. A. Winkler prepared the salt by crystallization from soln. of the component salts. The salt has a sharp, saline, and astringent taste; the transparent, octahedral crystals neither deliquesce nor effloresce in air; they give off ammonium chloride when heated, and are easily soluble in water, but not in alcohol when heated. The boiling soln. is reduced by zinc depositing metallic iron. A. Johnsen could not prepare the ammonium salt, although he once obtained  $\text{NH}_4\text{Cl} \cdot \text{FeCl}_2 \cdot 6\text{H}_2\text{O}$ , but he could not repeat his results. The formation of solid soln. of ammonium and ferrous chlorides was discussed by J. H. van't Hoff. F. W. J. Clendinnen studied the ternary system:  $\text{NH}_4\text{Cl}-\text{FeCl}_2-\text{H}_2\text{O}$  at  $70^\circ$ . That temp. was selected so as to eliminate hydrates higher than the dihydrate, but the tetrahydrate does appear at this temp. although it affects only a small portion of the equilibrium diagram,

Fig. 562. A continuous series of solid soln. is formed at the ammonium chloride end, but there is a gap near the ferrous chloride end of the system. For **ferrous hydrazinochloride**,  $\text{FeCl}_2 \cdot 2\text{N}_2\text{H}_4$ , *vide supra*. A. Chassevant prepared **lithium ferrous trichloride**, or *lithium trichloroferrite*,  $\text{LiCl} \cdot \text{FeCl}_2 \cdot 3\text{H}_2\text{O}$ , in transparent, green needles by evaporating a soln. of the component salts. In his study of the crystallization of mixed soln. of ferrous and potassium chlorides, H. E. Boeke observed that at  $38.3^\circ$ , **potassium ferrous trichloride**, or *potassium trichloroferrite*,  $\text{KFeCl}_3 \cdot 2\text{H}_2\text{O}$ , separates out; below this temp. potassium chloride and tetrahydrated ferrous chloride are deposited. H. E. Boeke did not succeed in preparing the **potassium ferrous tetrachloride**, or *potassium tetrachloroferrite*,  $\text{K}_2\text{FeCl}_4 \cdot 2\text{H}_2\text{O}$ , obtained by J. Schabus in bluish-green monoclinic crystals, by crystallization from a boiling soln. of three parts of potassium chloride, and four parts of ferrous chloride. The salt was prepared by A. Chassevant. A. Johnsen found that the monoclinic crystals have the axial ratios  $a : b : c = 1.0318 : 1 : 0.7066$ , and  $\beta = 89^\circ 40'$ . The optical axial angle  $2H = 88^\circ 3'$ ; the sp. gr. is 1.46; the index of refraction for Na-light is 1.4694, and for Li-light, 1.4721. The aq. soln. becomes turbid at  $105^\circ$ . H. E. Boeke found that the *dihydrate* is formed from a soln. of the component salts at  $38.3^\circ$ , and it is stable up to  $85^\circ$ . J. Fritzsche reported that it can be converted into the *monohydrate*; and A. Chassevant obtained the anhydrous salt. C. Ochsnius

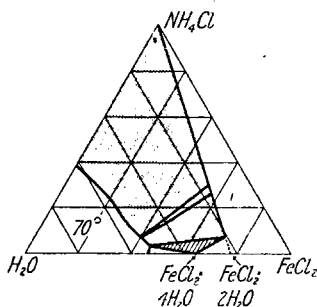


FIG. 562.—Equilibrium Diagram for the System:  $\text{NH}_4\text{Cl}-\text{FeCl}_2-\text{H}_2\text{O}$  at  $70^\circ$ .

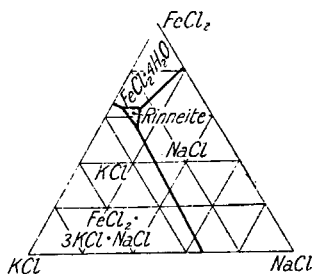


FIG. 563.—Ternary System:  $\text{FeCl}_2-\text{KCl}-\text{NaCl}$  at  $38.0^\circ$ .

and H. Precht reported this salt to be associated with the carnallite in the Douglasshall salt-mine at Stassfurt, and the mineral was called **douglasite**. The crystals are monoclinic, and their sp. gr. is 2.162. E. Wilke-Dörfurt and G. Heyne prepared **rubidium ferrous trichloride**, or *rubidium trichloroferrite*,  $\text{RbFeCl}_3 \cdot 2\text{H}_2\text{O}$ , in pale green, efflorescent crystals of sp. gr. 2.711 at  $20^\circ$ ; **rubidium ferrous tetrachloride**, or *rubidium tetrachloroferrite*,  $\text{Rb}_2\text{FeCl}_4 \cdot 2\text{H}_2\text{O}$ , in clear, monoclinic crystals of sp. gr. 2.850 at  $23^\circ$ , which effloresce and oxidize in air; **caesium ferrous trichloride**, or *caesium trichloroferrite*,  $\text{CsFeCl}_3 \cdot 2\text{H}_2\text{O}$ , in green, efflorescent crystals of sp. gr. 2.907 at  $17^\circ$ ; and **caesium ferrous tetrachloride**, or *caesium tetrachloroferrite*,  $\text{Cs}_2\text{FeCl}_4 \cdot 2\text{H}_2\text{O}$ , in colourless, efflorescent, monoclinic crystals of sp. gr. 3.275 at  $20^\circ$ . E. H. Ducloux discussed the micro-appearance of the double salt. No **sodium ferrous chloride** has been prepared, but, according to H. E. Boeke, **sodium tripotassium ferrous hexachloride**,  $3\text{KCl} \cdot \text{NaCl} \cdot \text{FeCl}_2$ , occurs in the salt-beds at Nordhausen, Saxony, in association with the carnallite and sylvite. The mineral was called **rinneite**—after F. Rinne. H. Jung gave the formula  $[\text{FeCl}_6]\text{K}_3\text{Na}$ . According to H. E. Boeke, rinneite occurs in coarsely granular masses of hexagonal crystals, with the cleavage, parallel to the prism, perfect. The crystals are colourless when fresh, but on exposure become green, rose, violet, yellow, and brown. The optical character is positive, and the birefringence is weak. C. W. Cheng gave for the axial ratios of the trigonal crystals  $a : c = 1 : 0.574$ . The corrosion figures correspond with the ditrigonal scalenohedral symmetry. The pyroelectricity is negative. The dimensions of the elementary rhombohedron

are  $a=8.40$  A., and  $\alpha=92^\circ 25'$ . The sp. gr. is 2.34, and the hardness 3. The salt oxidizes in air but is stable under petroleum. The hot, sat. aq. soln. deposits crystals of potassium chloride on cooling. H. E. Boeke found that a soln. containing the component salts in the molar proportions of rinneite, furnish that salt at  $26.4^\circ$ —*vide* Fig. 563. For the artificial preparation of the triple salt, a soln., obtained by dissolving 5.96 grams of sodium chloride, 20.9 grams of potassium chloride, and 123.4 grams of ferrous chloride ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ) in 55.4 grams of water, should be isothermally evaporated at  $38^\circ$  with the addition of a crystal of rinneite. According to R. Kremann and F. Noss, no **cuprous ferrous chloride** has been obtained, but, at  $21.5^\circ$ , the solubility of cuprous chloride is increased by the addition of ferrous chloride, as also that of ferrous chloride by the addition of cuprous chloride, the solid phases in equilibrium with the soln. being respectively cuprous chloride and ferrous chloride. The soln. sat. with respect to both the salts contains 73.20 grms. of ferrous chloride (anhydrous) and 23.20 grms. of cuprous chloride in 100 grms. of water.

A. Ferrari and A. Inganni found that with **calcium and ferrous chlorides** there is a eutectic at  $592^\circ$ , with 44.5 mol. per cent. of  $\text{CaCl}_2$ , Fig. 564. The results for **strontium and ferrous chlorides**, indicated in Fig. 565, show no miscibility in the solid state, and there is a eutectic at  $541^\circ$  and 50 mol. per cent. of ferrous chloride

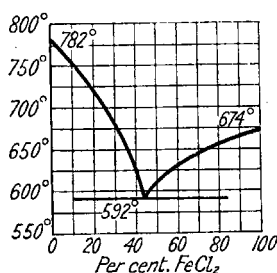


FIG. 564.—Freezing-point Curves of Ferrous and Calcium Chlorides.

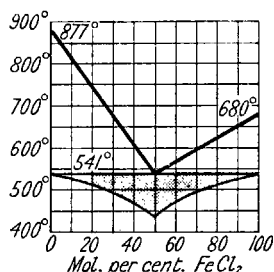


FIG. 565.—Freezing-point Curves of Ferrous and Strontium Chlorides.

H. E. Boeke studied the binary system with soln. of ferrous and magnesium chlorides, and the ternary system with soln. of potassium, magnesium, and ferrous chlorides. Tetrahydrated ferrous chloride, in contact with the sat. soln., forms the dihydrate at  $72.6^\circ$ , but in a sat. soln. of magnesium ferrous chloride, the dihydrate forms at  $43.2^\circ$ . Triclinic crystals of **magnesium ferrous tetrachloride**, or *magnesium tetrachloroferrite*,  $\text{MgFeCl}_4 \cdot 8\text{H}_2\text{O}$ , separate at  $22.8^\circ$ . The equilibrium conditions are illustrated by Figs. 566, 567, and 568. The common occurrence of ferric oxide in carnallite, which makes the colour of this mineral red, is generally explained by assuming that the oxide has been formed by the oxidation of ferrous chloride. H. Precht assumed that the oxidation was effected by the water of crystallization of carnallite and that hydrogen escaped; E. Erdmann could not find evidence in favour of such a reaction, and assumed that the oxidation was due to the mixture of hydrogen and oxygen formed by the action of radium emanation. A. Johnsen showed that the orientation of the plates of iron-mica in primary carnallite support H. Precht's assumption. Carnallite was shown by H. E. Boeke to have a small tendency to form isomorphous mixtures with ferrous chloride, and that ferric chloride has no such tendency. A. Ferrari and M. Carugati found that the crystal lattices of the system  $\text{FeCl}_2\text{--MgCl}_2$ .

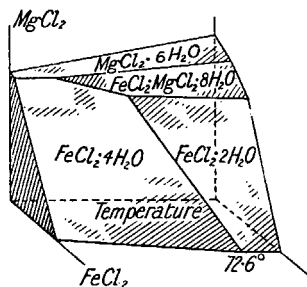


FIG. 566.—Equilibrium in the System:  $\text{FeCl}_2\text{--MgCl}_2\text{--H}_2\text{O}$ .

showed that a complete series of solid soln. is formed. The m.p. curve is shown in Fig. 566. A. Ferrari and A. Inganni observed no miscibility in the system

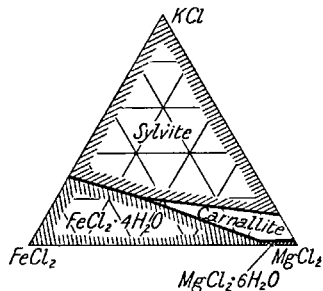


FIG. 567.—Equilibrium in the System :  $\text{FeCl}_2\text{-MgCl}_2\text{-KCl-H}_2\text{O}$  at  $22.8^\circ$ .

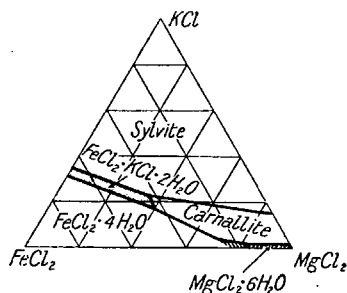


FIG. 568.—Equilibrium in the System :  $\text{FeCl}_2\text{-MgCl}_2\text{-KCl-H}_2\text{O}$  at  $43.2^\circ$ .

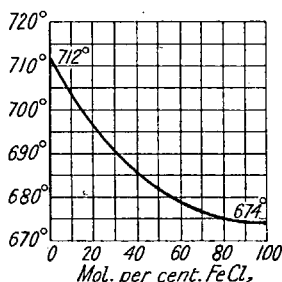


FIG. 569.—Freezing-point Curves of the System :  $\text{MgCl}_2\text{-FeCl}_2$ .

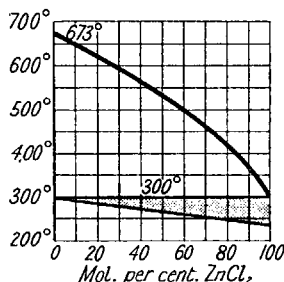


FIG. 570.—Freezing-point Curves of the System :  $\text{ZnCl}_2\text{-FeCl}_2$ .

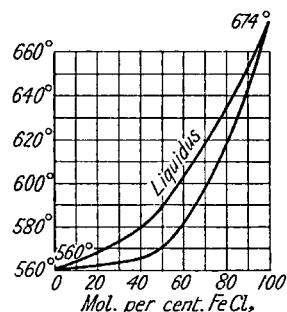


FIG. 571.—Freezing-point Curves of the System :  $\text{CdCl}_2\text{-FeCl}_2$ .

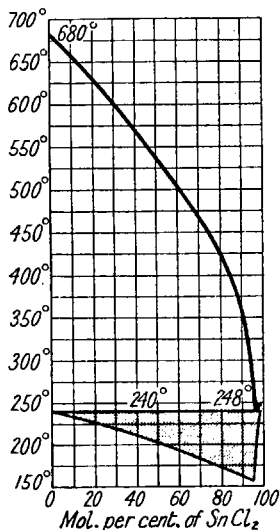


FIG. 572.—The System :  $\text{SnCl}_2\text{-FeCl}_2$ .

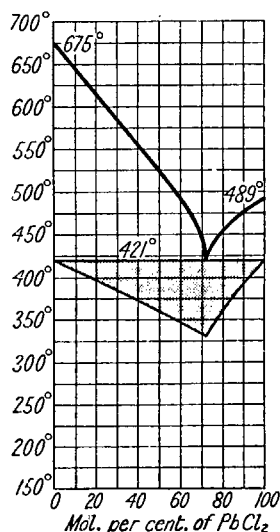


FIG. 573.—The System :  $\text{PbCl}_2\text{-FeCl}_2$ .

with **zinc and ferrous chlorides**, and the eutectic temp. is the same as the m.p. of zinc chloride, namely,  $300^\circ$ . C. von Hauer obtained colourless, non-efflorescent

crystals of **cadmium ferrous hexachloride**,  $2\text{CdCl}_2 \cdot \text{FeCl}_2 \cdot 12\text{H}_2\text{O}$ . A. Ferrari and M. Carugati found that the crystal lattices of the system  $\text{FeCl}_2$ - $\text{CdCl}_2$  show that a complete series of solid soln. is formed. The m.p. curve is shown in Fig. 571. P. A. von Bonsdorff prepared honey-yellow, deliquescent, rhombic prisms of **mercuric ferrous tetrachloride**,  $\text{HgCl}_2 \cdot \text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ —*vide supra*. E. Harbort described rhombohedral crystals of a hydrated **ferrous aluminium oxychloride**,  $9\{(\text{Fe}, \text{Mg}, \text{Ca})\text{Cl}_2 \cdot 2\text{H}_2\text{O}\} \cdot 2(\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O})$ , occurring in the German potash deposits. It was called **zirklerite**—after Bergrat Zirkler. E. von Biron prepared **stannic ferrous hexachloride**,  $\text{SnFeCl}_6 \cdot 6\text{H}_2\text{O}$ —*vide* 7. 46, 17. A. Ferrari and C. Colla studied the m.p. of the system:  $\text{SnCl}_2$ - $\text{FeCl}_2$ , and of the **lead-ferrous chloride** system. No compounds were formed. With the former system, Fig. 572, there is a eutectic at  $240^\circ$ , with about 2 mol. per cent. of  $\text{FeCl}_2$ ; and in the latter system, Fig. 573, one at  $421^\circ$  with 28.5 mol. per cent. of  $\text{FeCl}_2$ —m.p.  $675^\circ$  to  $680^\circ$ . R. F. Weinland and co-workers obtained **ferrous bismuth chloride**,  $\text{FeCl}_2 \cdot 4\text{BiCl}_3 \cdot 12\text{H}_2\text{O}$ , by the action of bismuth chloride on a hydrochloric acid soln. of ferrous chloride. A. Ferrari and co-workers examined isomorphous mixtures of **ferrous and manganous chlorides**, and found the X-radiograms agreed with  $\text{FeCl}_2 \cdot \text{MnCl}_2 = 8:2$ ,  $a = 7.16 \text{ \AA}$ ,  $a:c = 1:2.434$ ; for  $6:4$ ,  $a = 7.17 \text{ \AA}$ , and  $a:c = 1:2.419$ ; for  $4:6$ ,  $a = 7.18 \text{ \AA}$ , and  $a:c = 1:2.404$ ; for  $2:8$ ,  $a = 7.19 \text{ \AA}$ , and  $a:c = 1:2.387$ . The m.p. of mixtures of manganous and ferrous chlorides, plotted in Fig. 574, are:

$\text{FeCl}_2$	0	20	40	60	80	100 per cent.
M.p.	$650^\circ$	$652^\circ$	$656^\circ$	$661^\circ$	$668^\circ$	$674^\circ$

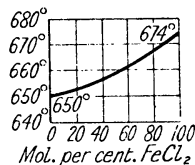


FIG. 574.—The Melting-points of Manganous and Ferrous Chlorides.

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### § 37. The Iron Chlorides—Ferric and Ferrous Chlorides

The history of ferric chloride is indicated in the previous section. In 1819, J. F. L. Hausmann<sup>1</sup> noticed a brownish-red incrustation on the lavas of Vesuvius, and A. Scacchi observed in recent eruptions a yellow or brownish-red incrustation associated with the lavas of fumaroles or steam holes. The coloration was attributed to the presence of **ferric chloride**,  $\text{FeCl}_3$ , and A. Scacchi called the mineral *molysite*, which J. D. Dana altered to **molysite**—from *μόλως*, a stain—in allusion to its staining the lavas. Drops of ferric chloride often exude from the surface of meteoric irons; A. Daubree called the drops *stigmatite*; they are formed by the oxidation of lawrencite (*q.v.*).

**The formation and preparation of ferric chloride.**—As pointed out by H. Davy,<sup>2</sup> J. Davy, J. J. Berzelius, R. Phillips, J. L. Gay Lussac, I. E. Adaduroff, M. Goble, F. Wöhler, A. W. F. Rogstad, etc., when a piece of red-hot iron is introduced into chlorine gas, the iron burns with a red glow forming ferric chloride. H. Davy said that the chloride which is formed volatilizes “at a moderate heat, filling the vessel with beautiful, minute crystals of extraordinary splendour and collecting in brilliant plates.” The same result occurs when a rapid current of dry chlorine is passed over iron wire, cut into short pieces, say, 6 mm., and gently heated in a retort. The ferric chloride volatilizes, and condenses in reddish crystals in the cooler part of the tube. The chlorine gas can then be displaced by a current of dry carbon dioxide, and the salt transferred to a tube, and hermetically sealed. Several books for the laboratory give detailed directions for the preparation of the salt—*e.g.*, those of H. and W. Biltz, L. Vanino, etc. The process was described by H. Wolfram, W. Hampe, F. W. Bergstrom, A. S. Miller, W. Grünwald and V. Meyer, and O. Hönigsmid and co-workers. H. C. Jones and C. F. Lindsay recommended using iron filings washed with alcohol and ether to remove fats; C. G. Maier recommended using electrolytic iron heated between 400° to 500°, and subliming the product three times in an atm. of chlorine at 300°. Sublimation in vacuo results in the dissociation of some of the ferric chloride to form ferrous chloride. B. H. Jacobson recommended treating iron with liquid bromine, and then decomposing the ferric bromide with chlorine. These reactions occur at a comparatively low temp.

A. Vosmaer found that ferrochromium or ferrotungsten, and J. Meyer and R. Backa that ferrovanadium, furnish ferric chloride when heated in chlorine gas—a chloride of the

second element is also formed. Ferric chloride was also produced by P. Nicolardot when liquid sulphur monochloride acts on iron; K. Ott, and H. B. North and A. M. Hageman obtained a similar result by the action of thionyl chloride at 150°; H. B. North, by the action of sulphuryl chloride; W. L. Ray, by the action of selenium oxydichloride; E. Baudrimont, and H. Goldschmidt, by the action of phosphorus pentachloride; and L. Hackspill and L. Grandadam, by the action of alkali chlorides at 800°.

J. L. Gay Lussac, E. Mitscherlich, and H. St. C. Deville obtained ferric chloride by passing a rapid current of dry hydrogen chloride over red-hot precipitated ferric oxide; with a slow current of gas, crystals of ferric oxide are formed by the action of the steam produced in the reaction:  $\text{Fe}_2\text{O}_3 + 6\text{HCl} \rightleftharpoons 3\text{H}_2\text{O} + 2\text{FeCl}_3$ . J. B. Moyer recommended using a temp. of 200°, and said that ferric chloride quickly volatilizes, leaving behind some less volatile ferrous chloride. F. A. Gooch and F. S. Havens observed that at 180° to 200°, about 5 to 10 per cent. of the oxide is converted into ferrous chloride; and at 500°, all the iron oxide is converted into ferric chloride. If a little chlorine is associated with the hydrogen chloride, all the ferric oxide is transformed to ferric chloride at 180° to 200°. The hydrogen chloride process, or a mixture of hydrogen and chlorine was employed on roasted iron ores by E. Diepschlag, A. and P. Buisine, the Vereinigte Stahlwerke, and F. Bullnheimer. R. Weber, and H. Schulze said that roasted iron ores, containing ferrous and ferric oxides, furnish ferric chloride when heated to redness in chlorine gas, M. Berthelot observed that the reaction between chlorine and ferrous oxide is exothermal, and with ferric oxide endothermal, but W. Kangro and R. Flügge added that at 700° to 800°, the reaction with ferric oxide and chlorine is exothermal. The reaction with precipitated oxide roasted at 1000° is perceptible at 600° and proceeds more quickly as the temp. is raised; at 1000°, magnetite, hæmatite, and minette ore are converted quantitatively into ferric chloride; and at 900°, oolitic earth, and ores of the xanthosiderite type. The Vereinigte Stahlwerke observed that by increasing the press. of the gas, the speed of the reaction is raised. E. Kothny observed the formation of ferric chloride in the chloridizing roasting of pyrites. H. Quantin, and F. P. Venable and D. H. Jackson found that ferric oxide is readily converted into ferric chloride by heating it to about 460° in a mixture of carbon monoxide and chlorine; the Badische Anilin- und Sodafabrik treated chromite, and E. W. Wescott, and H. Bergius treated roasted iron ores in a similar manner. E. Chauvenet, and W. Heap and E. Newbery converted ferric oxide to ferric chloride by heating it above 350° in a current of carbonyl chloride; and P. Camboulives used carbon tetrachloride above 245°; and R. D. Hall, sulphur monochloride. H. B. North and A. M. Hageman observed the formation of ferric chloride when ferric oxide is heated with thionyl chloride; W. L. Ray, with selenium oxydichloride; G. Rauter, with silicon tetrachloride, at 180° to 190°; R. Weber, with phosphorus pentachloride; and H. Bassett and H. S. Taylor, with phosphoryl chloride. H. Arctowsky found that ferric chloride is formed by passing the vapour of ammonium chloride over ferric oxide above 350°. The Vereinigte Stahlwerke used the same process with oxidized ores; H. Bergius heated the oxidized ore with carbon and sodium chloride; and K. A. Hofmann and K. Hösehele heated ferric oxide with molten magnesium chloride and obtained a sublimate of ferric chloride.

J. Davy observed that when ferrous chloride is heated in chlorine, it is quantitatively converted into ferric chloride; and the formation of ferric chloride by heating ferrous chloride in air has been previously discussed. D. Tyrer used a process based on this reaction. H. Rose observed that when chlorine is passed over heated iron sulphide, ferric chloride and sulphur monochloride are formed; and W. Kangro and R. Flügge found that the reaction with pyrite is rapid and complete at about 900°. The process was studied by R. Brandt, T. R. Forland, and E. W. Wescott. E. Chauvenet observed that pyrites forms ferric chloride when heated with carbonyl chloride at 350°, and E. F. Smith obtained a similar result with arsenopyrite, pyrite, and marcasite and liquid sulphur monochloride; H. B. North and C. B. Conover, with thionyl chloride in a sealed tube at 150°;

A. P. Brown, with ammonium chloride at  $335^{\circ}$ ; and H. Vater, with fused sodium chloride. C. Hensgen converted anhydrous ferrous sulphate into ferric chloride by heating it in a current of hydrogen chloride. A. Conduché obtained ferrous and ferric chlorides by the action of heated chloroform on ferrous or ferric sulphates. K. H. Oenicke observed no ferric chloride was formed from a mixture of sodium chloride and ferrous sulphate at a temp. at which sublimation occurs, but at a higher temp. ferric chloride is produced. A. Baur, and H. St. C. Deville and L. Troost prepared ferric chloride as a sublimate by heating a mixture of equal parts of dehydrated ferrous sulphate and calcium chloride. G. J. Fowler observed that iron nitride inflames spontaneously in chlorine forming ferric chloride and nitrogen; P. Jannasch and F. Schmidt, that ferric nitrate heated in hydrogen chloride at  $110^{\circ}$  to  $120^{\circ}$  forms a mixture of ferrous and ferric chlorides. W. Kangro and R. Flügge observed that ferrous phosphate at  $900^{\circ}$  is converted by chlorine into ferric chloride, the phosphorus remains in a non-volatile form. H. Quantin substituted carbon tetrachloride for chlorine, and obtained a quantitative chlorination of the iron. H. Schröder converted aluminium iron phosphates into volatile ferric chloride by heating them with calcium or magnesium chloride, or carnallite. F. Wöhler found that ferrous carbonate is converted by chlorine into ferric chloride, ferric oxide, and some ferrous chloride—W. Kangro and R. Flügge said the conversion can be completed at  $900^{\circ}$ . C. Friedel and J. Guérin observed that titanium chloride converts red-hot ferrous carbonate into ferric chloride, etc. W. Kangro and R. Flügge observed that chamosite, and iron aluminosilicate, at  $900^{\circ}$  is converted by chlorine into ferric chloride, etc. H. von Wartenberg noted that the iron in porcelain at  $1000^{\circ}$  to  $1100^{\circ}$  is attacked by chlorine; and F. W. Clarke and E. A. Schneider, that at  $400^{\circ}$ , only a little of the iron in iron-mica is converted into ferric chloride. For roasted silicates, etc., *vide supra*. C. Friedel and J. Guérin observed that chlorine passed over heated ferrous titanate yields ferric chloride quantitatively; and F. Wöhler, that ferrous tungstate under similar conditions yields ferric chloride and tungsten oxychloride.

Anhydrous ferric chloride is formed by the dehydration of the hydrated ferric chlorides. E. C. J. Mohr said that the dehydration does not occur at ordinary temp. over conc. sulphuric acid, but above  $50^{\circ}$ , the anhydrous salt is formed; and H. W. B. Roozeboom found that in soln. with over 84 per cent. of ferric chloride, the anhydrous salt is the stable form above  $66^{\circ}$ . A. Béchamp, J. J. Berzelius, J. B. A. Dumas, M. Goble, C. F. Mohr, and E. L. Schubarth heated the crystals of the hydrate very slowly and obtained a sublimate of ferric chloride. According to P. L. Hulin, the poor yields are due to hydrolytic changes and they can be avoided by heating the chloride in chlorine or hydrogen chloride.

**The hydrates of ferric chloride.**—The red liquid formed by the deliquescence of ferric chloride was formerly called *oleum martis*. C. W. Scheele observed that iron filings in moist chlorine dissolve to form a liquid. According to J. J. Berzelius, L. J. Thénard, C. F. Bucholz, M. Goble, B. Sandrock, P. J. Béal, A. and P. Buisine, and M. J. B. Orfila, an aq. soln. of ferric chloride is readily formed by dissolving ferric oxide, or hydrated ferric oxide, in hydrochloric acid; C. F. Mohr, F. Leteur, J. Fritzsche, and E. Soubeiran used powdered hæmatite. F. W. J. Clendinnen observed that the conc. soln. attacks filter-paper so that it is better to use fine silver gauze for the filtration. Ferric chloride is readily obtained by dissolving iron to saturation in hydrochloric acid, boiling the soln., and then oxidizing it with chlorine or nitric acid. J. E. de Vry, and B. Sandrock, oxidized the soln. of iron in hydrochloric acid by saturating the liquid with chlorine. J. W. Retgers pointed out that the reaction is slow at ordinary temp., and J. W. Retgers, F. W. C. Krecke, G. Krüss and H. Moraht, and F. A. Flückiger recommended warming the liquid to about  $50^{\circ}$  when it is treated with chlorine. A. Béchamp recommended removing the excess of chlorine by warming the liquid to  $50^{\circ}$ , and A. A. Noyes, and G. Krüss and H. Moraht, by passing a current of air through the liquid. The oxidation with chlorine on a large scale was recommended by F. Chemnitz, and D. Tyrer. The

oxidation of the soln. of iron in hydrochloric acid by nitric acid was recommended by F. L. Winckler, B. Sandrock, and E. L. Schubarth. F. A. Flückiger represented the reaction:  $3\text{FeCl}_2 + 3\text{HCl} + \text{HNO}_3 = 3\text{FeCl}_3 + \text{NO} + 2\text{H}_2\text{O}$ . J. E. de Vry pointed out the difficulty of removing the excess of nitric acid; a small excess may be driven off when evaporating the soln., but some nitric acid still contaminates the crystals. E. B. Shuttleworth stated that the oxidation proceeds more rapidly and completely if the soln. of ferrous chloride be added to the nitric acid than conversely—presumably owing to a better admixture.

The preparation of ferric chloride from by-products in the manufacture of other products, or for special purposes, was described by C. A. Burghardt, C. A. Hall, and L. Paul. Commercial preparations of anhydrous and hydrated ferric chloride were examined by M. Popp, J. C. Hostetter and H. S. Roberts, P. Piazza, C. H. Briggs, F. A. Flückiger, K. Feist, G. Romijn, and F. Richard and A. Malmy. The chief impurities observed were iron oxychloride, ferrous chloride, hydrochloric acid, nitrates, nitrites, chlorides, sulphates of copper, manganese, and zinc. R. Peters, H. W. Fischer and E. Brieger, R. Peters, and G. Schult discussed the preparation of clear, colourless, aq. soln. of ferric chloride by dissolving sublimed ferric chloride in water.

P. P. von Weimarn obtained a glassy, transparent, yellow or pale green gelatinous mass by the rapid cooling of a soln. of ferric chloride. Crystals of the **hexahydrate**,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , separate when the conc., aq. soln. of ferric chloride, acidified with hydrochloric acid, is allowed to stand in the cold. J. R. Glauber, and M. H. Klaproth probably obtained crystals of this hydrate in the seventeenth and eighteenth centuries. The crystals were also obtained by C. F. Bucholz, R. Engel, J. Fritzsche, W. Hampe, M. Kinast, C. F. Mohr, H. W. B. Roozeboom, P. Sabatier, G. Schult, C. Stein, and F. L. Winckler. The hexahydrate is obtained by saturating a soln. of ferric chloride with hydrogen chloride, and concentrating the filtered liquid over solid potassium hydroxide in vacuo; or by allowing the conc. soln. to evaporate slowly in the cold. The conditions of equilibrium are indicated in Fig. 575.

H. Lescœur concluded from his observations on the dissociation press. of the hydrates that a **tetrahydrate**,  $\text{FeCl}_3 \cdot 4\text{H}_2\text{O}$ , exists, but this has not been confirmed. According to H. W. B. Roozeboom, crystals of the **hemiheptahydrate**,  $\text{FeCl}_3 \cdot 3.5\text{H}_2\text{O}$ , are produced from a soln. of the composition  $\text{FeCl}_3 + 3.75\text{H}_2\text{O}$ , at room temp., by seeding it with a crystal of the same hydrate, pouring off the mother-liquor, melting the crystals, crystallizing the molten mass, and repeating the operations until a product of constant m.p. is formed. The crystals used for seeding can be obtained by melting together crystals of the hexa- and hemipentahydrates so that the composition approximates  $\text{FeCl}_3 + 4.12\text{H}_2\text{O}$ , solidifying the mass at room temp., and warming it to  $27^\circ$ . The solid which remains consists of crystals of the hemiheptahydrate. The conditions of stability are indicated in Fig. 575. Crystals of the **hemipentahydrate**,  $\text{FeCl}_3 \cdot 2.5\text{H}_2\text{O}$ , were probably formed by P. L. Geiger, M. Kinast, J. M. Ordway, C. Stein, and G. C. Wittstein, but they thought that they were crystals of the **trihydrate**,  $\text{FeCl}_3 \cdot 3\text{H}_2\text{O}$ , a hydrate whose existence has not been established. J. Fritzsche first reported the existence of the hemipentahydrate; he obtained it by keeping the hexahydrate over conc. sulphuric acid, when the mixture liquefies, and crystals of the hemiheptahydrate separate out, and finally, the whole mass acquires the same degree

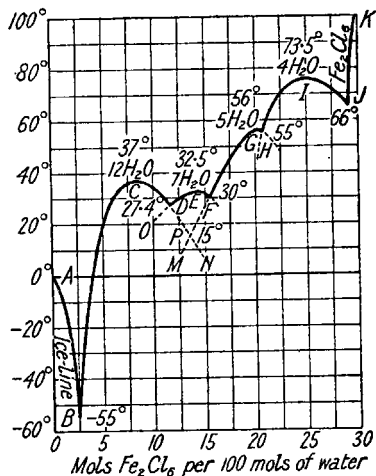


FIG. 575.—The Solubility of Ferric Chloride in Water.

of hydration. The results were confirmed by P. Sabatier, H. Lescœur, and E. C. J. Mohr. H. W. B. Roozeboom added that this hydrate is stable at room temp. over conc. sulphuric acid; and he obtained it by melting the hexahydrate on a water-bath, evaporating off about half the water of hydration, and crystallizing at room temp. The conditions of equilibrium are indicated in Fig. 575. Some hydrogen chloride is lost during the evaporation so that the crystals must be purified by re-melting and re-crystallizing them a number of times. R. Engel obtained this hydrate by passing hydrogen chloride over the hexahydrate for some hours at  $100^{\circ}$ , and slowly cooling the product. The resulting hemipentahydrate is free from oxychloride. H. W. B. Roozeboom obtained crystals of the **dihydrate**,  $\text{FeCl}_3 \cdot 2\text{H}_2\text{O}$ , from a soln. of anhydrous ferric chloride in the molten hemipentahydrate at a temp. exceeding  $56^{\circ}$ . The conditions of equilibrium are illustrated in Fig. 575. The product can be purified by repeatedly crystallizing the molten mass. If the dihydrate is melted in glass vessels, they are nearly always broken when the salt solidifies; and it is preferable to use a mortar for the purification of the salt by fusion and crystallization. H. W. B. Roozeboom and F. A. H. Schreinemakers obtained the dihydrate by passing hydrogen chloride over the hemipentahydrate. H. W. B. Roozeboom obtained the dihydrate by exposing one of the higher hydrates to an atm. where the press. of the water vapour is below 0.1 mm., and it is therefore not formed when the hemipentahydrate is kept over conc. sulphuric acid.

The hydrates of ferric chloride were studied by H. W. B. Roozeboom in the light of the phase rule, and the results are summarized in Fig. 575. The solubilities, S grms. of anhydrous chloride per 100 grms. of water, of the different hydrates are as follow:

The *hexahydrate*,  $\text{Fe}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$ , or  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,

	$-55^{\circ}$	$0^{\circ}$	$20^{\circ}$	$30^{\circ}$	$37^{\circ}$	$30^{\circ}$	$27.4^{\circ}$	$20^{\circ}$	$8^{\circ}$
S .	49.52	74.39	91.85	106.8	150.0	201.7	219.0	231.1	246.7

The *hemiheptahydrate*,  $\text{Fe}_2\text{Cl}_6 \cdot 7\text{H}_2\text{O}$ , or  $\text{FeCl}_3 \cdot 3\frac{1}{2}\text{H}_2\text{O}$ ,

		$20^{\circ}$	$27.4^{\circ}$	$32^{\circ}$	$32.5^{\circ}$	$30^{\circ}$	$25^{\circ}$
S .		204.4	218.7	244.0	257.6	272.4	280.0

The *hemipentahydrate*,  $\text{Fe}_2\text{Cl}_6 \cdot 5\text{H}_2\text{O}$ , or  $\text{FeCl}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ ,

	$12^{\circ}$	$20^{\circ}$	$27^{\circ}$	$30^{\circ}$	$35^{\circ}$	$50^{\circ}$	$55^{\circ}$	$56^{\circ}$	$55^{\circ}$
S .	231.8	251.2	267.5	272.3	281.6	315.2	344.8	360.4	365.9

The *dihydrate*,  $\text{Fe}_2\text{Cl}_6 \cdot 4\text{H}_2\text{O}$ , or  $\text{FeCl}_3 \cdot 2\text{H}_2\text{O}$ ,

	$50^{\circ}$	$55^{\circ}$	$60^{\circ}$	$69^{\circ}$	$72.5^{\circ}$	$73.5^{\circ}$	$72.5^{\circ}$	$70^{\circ}$	$66^{\circ}$
S .	359.3	365.9	372.8	387.7	420.5	450.2	470.8	502.4	525.9

The anhydrous chloride:

	$66^{\circ}$	$70^{\circ}$	$75^{\circ}$	$80^{\circ}$	$100^{\circ}$
S .	525.9	529.8	511.4	525.9	535.8

E. Kordes discussed the eutectics of the system. Hydrates reported by J. L. C. Schröder van der Kolk, and J. W. Retgers were shown by E. C. J. Mohr to be solid soln. with ammonium chloride. H. C. Jones and F. H. Getman obtained the percentage solubility,  $S=31.66$  at  $-51^{\circ}$ ; H. Mosler,  $32.62$  at  $-47.8^{\circ}$ ; G. Malquori,  $42.66$  at  $0^{\circ}$ ;  $49.76$  at  $25^{\circ}$ ;  $73.79$  at  $35^{\circ}$ ; and  $78.86$  at  $60^{\circ}$ ; E. C. J. Mohr,  $49.72$  at  $25^{\circ}$ ;  $54.61$  at  $35^{\circ}$ ; Y. Osaka and T. Yaginuma,  $49.42$  at  $25^{\circ}$ ; and F. W. J. Clendinnen,  $78.42$  at  $60^{\circ}$ . G. Lemoine said that the solubility at  $13^{\circ}$  corresponds approximately with a 4-molar soln.

According to H. W. B. Roozeboom, the metastable states are represented by dotted lines in Fig. 575. It will be observed that if a line be drawn in the diagram to represent a fixed temp., a little above  $30^{\circ}$ , it will intersect the solubility curve four times, and the points of intersection represent four different compositions for the sat. soln. at that temp. The eutectic between ice and the hexahydrate is at

—55°. The metastable eutectic between the hexahydrate and the hemipentahydrate is at 15°; the eutectic between the hexahydrate and the hemiheptahydrate is at 27.4°; the eutectic between the hemiheptahydrate and the hemipentahydrate is at 30°; the eutectic between the hemipentahydrate and the dihydrate is at 55°; and that between the dihydrate and the anhydrous salt is at 66°.

**The physical properties of ferric chloride.**—J. Königsberger and K. K  pferer noted that the colour of the vapour of ferric chloride at 250° is yellowish-brown. C. Friedel and J. M. Crafts also noted the intense colour of the vapour. H. Arctowsky said that molten ferric chloride is a red, mobile liquid. E. F. Smith said that the crystals obtained from soln. in sulphur monochloride are olive-green; and H. B. North and co-workers obtained for soln. in thionyl and sulphuryl chlorides, plates which were garnet-red in transmitted light, and green in reflected light. The **crystals** of the sublimed salt, said J. Davy, H. Davy, and J. L. Gay Lussac, occur in iron-black, iridescent scales; J. Goble said that they are dark violet; O. H  nigschmid and co-workers, reddish-brown—in masses almost black; E. Stirnemann, dark green; A. Neuhaus, deep carmine red; H. St. C. Deville, garnet-red in transmitted light and dark green in reflected light; and W. Gr  newald and V. Meyer, purple-red in transmitted light and dark green in reflected light. E. C. J. Mohr found that when obtained by keeping the hydrate over sulphuric acid above 50°, six-sided, reddish-brown plates are formed which in masses appear to be black with a green sheen. H. Arctowsky found that the crystals obtained from molten mixtures are purple-red in transmitted light and dark green in reflected light; and A. E. Nordenskj  ld obtained six-sided plates belonging to the hexagonal or triclinic system with axial ratios approximating  $a:c=1:1.235$ . E. Stirnemann said that the crystals are trigonal. V. M. Goldschmidt and co-workers, W. Nowacki, and P. Niggli and W. Nowacki discussed the space-lattice of the crystals of the anhydrous salt. H. Hansen showed that the lattice structure of ferric chloride probably consists of individual mol. groups, and that the energy required to break up the lattice is smaller than that required to dissociate the mol. groups. N. Wooster found that the unit rhombohedral cell is  $a=6.69$  A., and  $c=52^\circ 30'$ , or a hexagonal cell with  $a=5.92$  A., and  $c=1.26$  A. There are two molecules per unit rhombohedral cell, or six molecules per hexagonal cell. The crystals are isomorphous with those of bismuth triiodide.

According to F. A. Fl  ckiger, the crystals of the hexahydrate have a bitter, salty taste if free from hydrochloric acid. The descriptions of the hexahydrate by A. Benrath, R. Engel, F. A. Fl  ckiger, J. Fritzsche, W. Hampe, J. M. Ordway, P. Sabatier, and F. L. Winckler agree that it furnishes reniform masses of lemon-yellow, or pale yellow crystals, or opaque rhombic prisms or plates which, according to H. W. B. Roozeboom, are monoclinic. A. Neuhaus said that in 2 mm. layers, the crystals are pale yellowish-brown and pleochroic—yellow and yellowish-brown. The subject was also discussed by J. W. Retgers, and E. C. J. Mohr. H. W. B. Roozeboom said that the hemiheptahydrate forms monoclinic crystals which are darker in colour than the hexahydrate, and unlike the hexahydrate are dichroic with colours ranging from yellow to blue. A. Neuhaus said that the crystals in 2 mm. layers are dark yellowish-brown, and pleochroic—yellowish-brown to steel-grey. E. C. J. Mohr added that the pleochroism and crystallizing force of this hydrate are not so strong as in the case of the hemipentahydrate. J. L. C. Schr  der van der Kolk said that the double refraction of the crystals of the hemiheptahydrate is positive. R. Engel observed that the crystals of the hemipentahydrate obtained by slow cooling of soln. in hydrochloric acid are garnet-red. A. Neuhaus said that the crystals in 2-mm. layers are dark reddish-brown, and pleochroic—medium to dark reddish-brown. H. W. B. Roozeboom said that the rhombic crystals of the dihydrate are paler red than those of the hemipentahydrate, and that they are pleochroic with a colour ranging from yellow to brown. A. Neuhaus said that the crystals in 2-mm. layers are dark red, and pleochroic—yellowish-red to dark red.



The colour of conc. soln. of ferric chloride ranges from dark yellowish-brown to a reddish-brown; dil. soln. are yellow, and with very dil. soln. the yellow colour may disappear with ageing owing to hydrolysis which results in the formation of colloidal ferric oxide and hydrochloric acid. The colour of the soln. was discussed by C. F. Schönbein; the relation between the colour and conc. of the soln., by F. G. Donnan and H. Bassett, M. G. Mellon, M. Neidle, S. U. Pickering, M. Schneider, and H. M. Vernon; the effect of hydrolysis, and temp., by P. Apery, F. A. Flückiger, E. J. Houstoun, J. G. MacGregor, E. Schaer, T. Svedberg, and H. M. Vernon; and the use of the soln. as a colour scale in colorimetry, etc., by W. Crookes and co-workers, and H. V. Arny and co-workers. According to K. S. Ritchie, the exposure to sunlight or other sources of intense light of hydrochloric acid soln. of ferric chloride results in an increase in intensity of the colour of the soln.; on removal of the light the soln. slowly return to their initial condition. The fraction of incident light transmitted during a given exposure reaches a maximum near the commencement of the yellow region of the spectrum and falls rapidly to the green. Increased light absorption also results from heating a soln. of ferric chloride. P. P. von Weimarn observed that at liquid air temp., the colour becomes paler yellow or green as the soln. freezes to a glassy mass, conversely, F. A. Flückiger observed that a soln. almost colourless by dilution becomes distinctly yellow when warmed. The colour of conc. soln. is not perceptibly affected by hydrochloric acid, but dil. soln. become yellowish-green; the subject was discussed by H. V. Arny and co-workers, A. Byk and H. Jaffe, F. G. Donnan and H. Bassett, J. C. Hostetter, C. Hüttner, A. Müller, F. Mylius and A. Mazzucchelli, C. R. C. Tichborne, and H. M. Vernon; the effect of sulphuric acid, and alkali sulphates, chlorides of sodium, potassium, ammonium, calcium, and barium, and boric acid, by J. C. Hostetter; sodium and ammonium chlorides, by A. Müller; ammonium, sodium and antimony chlorides, by F. A. Flückiger; calcium and aluminium chlorides, by H. C. Jones and J. A. Anderson; ammonium chloride and potassium bromide, by E. Schaer; and of sulphuric, nitric, and phosphoric acids, and some organic acids and acid phosphates, by V. Macri.

According to H. St. C. Deville and L. Troost, the **vapour density** of ferric chloride is 11.14 at 440°, 11.01 at 619° (air unity). This is in agreement with the **molecular weight** of the salt with the formula  $\text{Fe}_2\text{Cl}_6$ . C. Friedel and J. M. Crafts, E. Stirnemann, and H. Biltz and F. Meyer showed that between 321.6° and 442.2°, in an atm. of chlorine, the vap. density is virtually constant and is in agreement with the doubled formula  $\text{Fe}_2\text{Cl}_6$ . Above 500°, the effects of the dissociation  $\text{Fe}_2\text{Cl}_6 \rightleftharpoons 2\text{FeCl}_3$  appear. E. Stirnemann found that at 253°, 271°, 285°, and 295°, a litre of the vapour contained respectively 0.3391, 0.9826, 0.302, and 3.43 grms. of  $\text{Fe}_2\text{Cl}_6$  per litre, corresponding respectively with mol. wts. from 322.4 to 337.0 when the value for  $\text{Fe}_2\text{Cl}_6$  is 324.4, and for  $\text{FeCl}_3$  162.2. For the dissociation:  $\text{Fe}_2\text{Cl}_6 \rightleftharpoons \text{Fe}_2\text{Cl}_4 + \text{Cl}_2$ , *vide infra*. At high temp. there is also the dissociation:  $\text{Fe}_2\text{Cl}_4 \rightleftharpoons 2\text{FeCl}_2$ . This explains the low results:

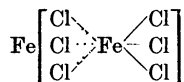
	448°	518°	606°	750°	1050°	1328°
Vapour density . . .	10.487	9.569	8.383	5.458	5.307	5.160

obtained by H. Biltz and V. Meyer, and W. Grünwald and V. Meyer working with an atm. of chlorine. A. Scott obtained a value 136.1 for the mol. wt. in an atm. of nitrogen.

D. I. Mendeléeff found that with soln. of ferric chloride in *water*, the rule that the sp. gr. of equimolar soln. is greater, the higher the mol. wt. of the solute is valid provided the doubled molecule  $\text{Fe}_2\text{Cl}_6$  is present. R. Peters showed that the lowering of the f.p. of *N*- to 0.0625*N*-soln. of ferric chloride corresponds with mol. wts. falling from 49.4 to 43.7. This indicates that some hydrolysis as well as ionization occurs. In some non-aqueous soln. there is a marked polymerization of the molecule. G. Oddo, G. Oddo and M. Tealdi, and E. Beckmann found that in *phosphoryl chloride* soln. with 0.5307 to 1.8426 grms. of  $\text{FeCl}_3$  in 100 grms. of solvent the mol. wt. ranged from 63.67 to 135.07; P. T. Muller, and E. Beckmann

found that the mol. wt. of the salt in boiling *ethyl alcohol* soln. is not far from normal, but there is some evidence of polymerization, thus E. Beckmann found for soln. with 2.37, 6.66, and 11.57 grms.  $\text{FeCl}_3$  in 100 grms. of solvent, the respective mol. wts. 195, 176, and 163. The mol. wt. in boiling *ethyl ether* was found by E. Beckmann to vary from 170 to 175 with soln. ranging from 1.53 to 12.70 grms. of  $\text{FeCl}_3$  per 100 grms. of solvent. Observations were also made by P. T. Muller, R. Lespieau, and J. Timmermans. The results are near those required for simple molecules, but there is evidence of polymerization; W. E. S. Turner found the mol. association factor to be 1.0 to 1.11. J. Timmermans found that for soln. with 1.228 to 3.125 grms.  $\text{FeCl}_3$  per 100 grms. of boiling *acetone*, the mol. wt. fell from 140 to 107.21, and he observed that in conc. soln., an oxychloride is formed; the mol. wt. of 0.589 gm.  $\text{FeCl}_3$  in 100 grms. of boiling *chloroform* is 153.9; 0.676 gm.  $\text{FeCl}_3$  in 100 grms. of *acetic acid* has a mol. wt. of 82.4; with 1.001 to 1.26 grms. of  $\text{FeCl}_3$  in 100 grms. of *sulphonal*, the mol. wt. is 174 to 197.9; with 0.659 to 1.056 grms.  $\text{FeCl}_3$  in 100 grms. of *benzophenone*, the mol. wt. ranges from 289.35 to 210.72; and with 0.593 to 2.213 grms.  $\text{FeCl}_3$  in 100 grms. of *benzoic acid*, the mol. wt. ranged from 179.9 to 211.86. E. Busch found that with 6.02 to 12.89 grms. of  $\text{FeCl}_3$  in 100 grms. of *methylal*, the mol. wt. ranged from 116 to 145; E. Beckmann, that in benzil, the mol. wt. indicates some polymerization; A. Werner and W. Schmujiöff, with 0.38 to 2.07 grms.  $\text{FeCl}_3$  in 100 grms. of boiling *pyridine*, the mol. wt. ranged from 146.05 to 150.05; and L. Kahlenberg and A. T. Lincoln, with 1.4792 to 4.7389 grms. of  $\text{FeCl}_3$  in 100 grms. of *nitrobenzene*, the mol. wt. ranged from 316.9 to 190.8; and J. Timmermans observed that with nitrobenzene, the mol. wt. decreases with increasing concentration of the soln.

There are no grounds for assuming that the iron in ferric chloride,  $\text{Fe}_2\text{Cl}_6$ , is quadrivalent, although the mol. wt. of the salt calculated from the vap. density in an atm. of chlorine corresponds with this formula. Writers on the co-ordination theory—R. Weinland, P. Pfeiffer, and A. Werner—regard this polymerized form as a ferric salt of *hexachloroferric acid*, namely:



A. Werner represented the hexahydrate by the formula for *ferric hexaquochloride*,  $[\text{Fe}(\text{H}_2\text{O})_6]\text{Cl}_3$ ; and R. Weinland suggested that by analogy with other hydrates, the colour of the salt rather favours the assumption that the hexahydrate is *ferric chloropentaquochloride*,  $[\text{Fe}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ , or else *ferric dichlorotetraquochloride*,  $[\text{Fe}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ . The subject was discussed by R. Reinicke, and H. Hansen.

According to J. P. Grabfield, the **specific gravity** of crystals of anhydrous ferric chloride is 2.804 at  $10.8^\circ/4^\circ$ ; K. Grossmann gave 2.804; and W. Biltz and E. Birk, 2.898 at  $25^\circ/4^\circ$ . A. Balandin calculated 2.844 for the sp. gr. from the relation between the density, the at. vol. of the components, and the heat of formation of the salt. A. Balandin, I. I. Saslawsky, and H. H. Stephenson discussed the contraction which occurs when the salt is formed from its components; and W. Biltz, and H. W. Fischer, the mol. vol. A. Heydweiller gave for the sp. gr. of soln. with *C* mols of  $\text{FeCl}_3$  per litre at  $18^\circ/4^\circ$ :

<i>C</i>	1	2	3	4	5	6	7	8
Sp. gr.	1.02263	1.04456	1.0870	1.1284	1.1690	1.2090	1.2486	1.3270

Observations on the sp. gr. of aq. soln. have also been made by H. Becquerel, A. Blümcke, F. W. J. Clendinnen, B. Franz, K. Grossmann, H. Hager, H. C. Jones and co-workers, A. Kanitz, G. Lemoine, W. Manchot and co-workers, G. Quincke, and G. Schult. E. Moles and co-workers obtained these results:

$\text{FeCl}_3$ (per cent.)	0.4088	1.6976	8.737	16.199	25.729	43.579	Sat.
Sp. gr. $\begin{cases} 0^\circ & . & 1.0035 & 1.0139 & 1.0774 & 1.1498 & 1.2465 & 1.4705 & — \\ 18^\circ & . & 1.0022 & 1.0121 & 1.0740 & 1.1451 & 1.2411 & 1.4654 & — \\ 25^\circ & . & 1.0003 & 1.0106 & 1.0718 & 1.1428 & 1.2381 & 1.4611 & 1.7934 \\ 35^\circ & . & 0.9976 & 1.0075 & 1.0684 & 1.1390 & 1.2339 & 1.4548 & 1.7849 \end{cases}$							

G. Quincke gave for the sp. gr. of soln. of 11.53, 18.89, 32.94, 48.07, and 54.83 per cent. ferric chloride in methyl alcohol, at 18° to 20°, respectively 0.8928, 0.9638, 1.1335, 1.4177, and 1.5374; A. Blümcke gave for soln. with 5.12, 10.00, 14.30, 12.00, and 32.10 per cent. of ferric chloride the respective sp. gr., at 15° to 19°, 0.836, 0.873, 0.903, 0.963, and 1.063. P. Schulz, and A. Naumann gave 1.1603 for the sp. gr. of a sat. soln. of ferric chloride in acetone at 18°/4°. H. Hager represented the change in the sp. gr. which attends a rise of 1° with soln. between :

FeCl <sub>3</sub> .	10 to 19	20 to 29	30 to 39	40 to 44	45 to 49	50 to 60 per cent.
Change .	0.0003	0.0004	0.0005	0.0006	0.0007	0.0008

P. F. Gaehr said that the relation between the sp. gr.  $D$ , and the concentration  $C$  per cent. can be represented by  $\log_{10} D = mC$ , where  $m$  is a constant; D. I. Mendeléeff discussed the relation between the sp. gr. and the mol. wt. of the salt in soln.; A. Taffel, the temp. of maximum density; F. W. C. Krecke, the effect of hydrolysis on the sp. gr.; R. Reinicke, the vol. relations of the water of crystallization; G. Beck, and I. I. Saslawsky, the mol. contraction; and A. Kanitz, and B. Cabrera and E. Moles, the effect of hydrochloric acid on the sp. gr. K. Grossmann found that the contraction  $\delta v$  which occurs when  $p$  per cent. of FeCl<sub>3</sub> is dissolved in unit vol. of water is nearly proportional to  $p$  so that  $\delta v/p$  is approximately constant. He found :

$p$ .	1.58	7.14	10.00	17.335	20.00	24.00	32.00 per cent.
$\delta v$ .	0.0034	0.0122	0.017	0.027	0.031	0.038	0.052

The rate of **diffusion** of ferric chloride in aq. soln. was examined by T. Graham, and M. Torre. L. Vanzetti showed that the diffusion of the salt is accompanied by hydrolysis; and I. D. Götz and G. P. Pamfil measured the speed of diffusion of soln. of ferric chloride in water, and in soln. of sodium nitrate. They concluded that the degree of hydration is not affected by the presence of strong electrolytes. The speed of diffusion of the salt in gelatin was examined by R. E. Liesegang, and H. R. Proctor and D. J. Law. T. Redwood found that ferric chloride in aq. soln. readily diffuses through a membrane, and T. Graham, A. Kossel, and P. Nicolardot showed that during the **osmosis** of a soln. of ferric chloride in a dialyzer, hydrolysis occurs, and while hydrochloric acid passes through the membrane, colloidal ferric hydroxide remains. H. G. Byers and C. H. Walter studied the so-called electro-endosmosis.

G. Quincke measured the **surface tension** of soln. of ferric chloride and found it to be smaller than that of water. H. Piepenstock represented the lowering of the surface tension of water, in percentages of  $\sigma$ , the value for water alone being such that the lowering  $a = 100(\delta\sigma/\sigma)/M$ , when  $\delta\sigma$  is the difference in the surface tensions of water and of the aq. soln.,  $M$  denotes the number of eq. FeCl<sub>3</sub> per litre of soln. The concentration of the soln. is expressed in percentages, the temp. approximated 18° :

$C$ .	6.83	9.24	12.00	14.56	17.58	22.19	25.40	28.79 per cent.
$a$ .	1.92	1.86	1.73	1.71	1.69	1.51	1.43	1.38

The lowering per eq. of ferric chloride in soln. decreases with increasing concentration. The influence of a magnetic field on the surface tension of the soln. was examined by P. Drapier, G. Quincke, and O. Liebknecht and A. P. Wills. W. L. Rolton and R. S. Troop observed that a magnetic field of 16,000 gauss had no perceptible influence on the surface tension of soln. of ferric chloride; L. Abonnenc also obtained a negative result; and D. Owen said that the theoretical change amounts to one in  $5 \times 10^6$  of the total surface tension by the action of a field of 20,000 gauss. O. Lorant observed that the limiting surface between ethyl ether, chloroform, and nitrobenzene, and an aq. soln. of ferric chloride is greater than is the case with water. G. Quincke made observations on the surface tension and sp. cohesion of soln. in methyl alcohol.

P. de Heen measured the fluidity of soln. of ferric chloride and the results were

discussed by C. Montigny. A. E. Oxley measured the velocity of flow of conc. soln. of ferric chloride at temp. between 0° and 80°. A. Kanitz observed that soln. of ferric chloride have a greater **viscosity** than is usual with soln. of other chlorides. W. Herz calculated from A. Kanitz's measurements of the viscosity,  $\eta$ , of *N*-, 0.5*N*-, 0.25*N*-, and 0.125*N*-FeCl<sub>3</sub> at 25°, respectively 0.01147, 0.01014, 0.00949, and 0.00922 c.g.s. units. E. Moles and co-workers obtained for soln. with :

FeCl <sub>3</sub> (per cent.)	0.4088	1.6975	8.737	16.199	25.729	43.579	Sat.
0° . . .	0.018299	0.019285	0.026489	0.039370	0.071170	0.35208	—
18° . . .	0.010750	0.011290	0.015380	0.022270	0.037440	0.13770	—
25° . . .	0.009125	0.009555	0.013040	0.018550	0.030510	0.10515	0.3164
35° . . .	0.007371	0.007742	0.010358	0.014488	0.023238	0.07202	0.1942

A. Smits and co-workers observed that, at 40°, the viscosity increased with the concentration up to 55.4 per cent. FeCl<sub>3</sub>, it then fell to a minimum with 62.5 to 65.0 per cent. FeCl<sub>3</sub>, and thereafter increased rapidly and continuously. The maximum and minimum points correspond very nearly with the hexahydrate and the hemiheptahydrate respectively. The subject was discussed by W. P. Jorissen; and the temp. coeff. of the viscosity by A. E. Oxley. A. Kanitz found that the addition of increasing proportions of hydrochloric acid to the soln. lowers the viscosity, due, it is supposed, to a reduction in the percentage hydrolysis. The effect of hydrolysis on the viscosity was discussed by E. Moles and co-workers, and Wo. Ostwald; and L. Abonnenc found that a magnetic field had no perceptible influence on the viscosity of soln. of ferric chloride.

The **thermal expansion** of soln. can be calculated from the observations of E. Moles and co-workers, and H. Hager on the effect of temp. on the sp. gr. of the aq. soln. O. Hülsmann and W. Biltz made observations on the subject. W. Beetz showed that the **thermal conductivity** of a soln. of sp. gr. 1.126 at 8° to 14° is greater than that of water, and that of a soln. of sp. gr. 1.244 at 8° to 14° is also greater than that of water. The conductivity of dil. soln. between 28° and 36° is smaller than that of water. W. Beetz examined the thermal conductivity of soln. in ethyl alcohol, and ether. A. Blümcke found that the **specific heat** of anhydrous ferric chloride is 0.145 at room temp.; and for 20, 28.8, and 43.56 per cent. aq. soln., respectively 0.813, 0.745, and 0.670. G. Lemoine found the sp. ht. of 3*M*-FeCl<sub>3</sub>, of sp. gr. 1.368, to be 0.66. The subject was studied by N. de Kolossowsky. A. Blümcke examined the sp. ht. of soln. in ethyl alcohol.

A. Brann, and J. H. Walton and A. Brann studied the **rate of crystallization** of aq. soln. of ferric chloride. H. W. B. Roozeboom said that owing to the low temp. of formation of the cryohydrate, -55°, the hexahydrate should make a good freezing mixture with ice, and he obtained -25° by this means. The **lowering of the freezing-point** of water by ferric chloride is indicated by the ice-line in Fig. 575, where H. W. B. Roozeboom found the f.p. of water with 18.01, 34.21, and 42.68 grms. of FeCl<sub>3</sub> per 100 grms. of water to be respectively -10.0°, -27.5°, and -40°, corresponding with the respective mol. lowerings of 9.0°, 13.0°, and 15.2°. H. Mosler found the f.p. of soln. of ferric chloride to be :

FeCl <sub>3</sub> . . .	10.3	23.0	28.5	33.1	38.5	43.4 per cent.
F.p. . . .	-5.7°	-15.8°	-22.0°	-27.2°	-36.8°	-47.8°

Observations were also made by F. M. Raoult, G. Malfitano and L. Michel, A. A. Noyes, N. Sasaki, and H. C. Jones and co-workers. R. Peters observed for :

FeCl <sub>3</sub> . . .	<i>N</i> -	0.5 <i>N</i> -	0.25 <i>N</i> -	0.125 <i>N</i> -	0.0625 <i>N</i> -
F.p. . . .	2.17°	1.02°	0.51°	0.263°	0.145°
$\alpha$ . . . .	0.82	0.76	0.74	0.80	0.84

The corresponding mol. wts. range from 49.4 to 43.7 showing that the ionization of ferric chloride in aq. soln. can be represented by  $\text{FeCl}_3 \rightleftharpoons \text{Fe}^{+++} + 3\text{Cl}^-$ . H. C. Jones and F. H. Getman noted that the mol. lowering of the f.p. passes through a

minimum form of concentration between 0.1 and 0.2 molar; thus, representing the concentration in mols per litre, the mol. lowerings of the f.p.,  $\Delta$ , are:

$C$	0.064	0.103	0.129	0.257	0.515	1.287	1.544	2.573
$\Delta$	6.05	5.89	5.87	6.14	7.16	10.06	11.40	19.82

G. Malfitano, and G. Malfitano and L. Michel discussed the influence of hydrolysis on the results; they observed that the lowering of the f.p.,  $\Delta$ , of a soln. of 5 grms. of  $\text{FeCl}_3$  per litre is  $\Delta=0.200$ ; after heating 15 mins. at  $115^\circ$  to  $120^\circ$ ,  $\Delta=0.300$ ; and after being kept for a long time at ordinary temp.,  $\Delta=0.270$ . A. A. Noyes found that the lowering of the f.p. of conc. soln. is affected additively by the introduction of hydrochloric acid, but with dil. soln. there is a deviation from the additive law which can be explained by the driving back of the hydrolysis by the acid. The **raising of the boiling-point** of various soln. has been discussed above in connection with the mol. wt. of the salt in soln.

T. Carnelley and W. C. Williams gave  $306^\circ$  to  $307^\circ$  for the **melting-point** of the anhydrous chloride; C. Friedel and J. M. Crafts gave  $280^\circ$  to  $285^\circ$ , and added

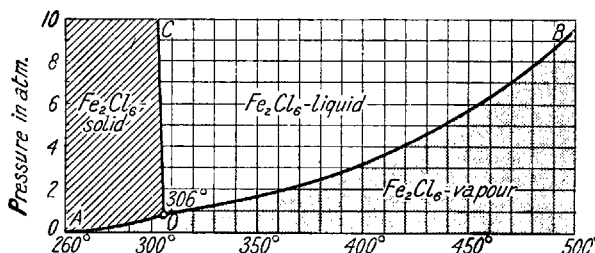


FIG. 576.—The Vapour Pressure of Ferric Chloride.

that it volatilizes at the same time; G. Herrmann gave  $298^\circ$ ; E. Stirnemann,  $306^\circ$ ; G. Scarpa,  $302^\circ$ ; and K. Hachmeister,  $303^\circ$ . E. Stirnemann's value,  $306^\circ$ , is at the junction of the sublimation and b.p. curve, Fig. 576. O. Hönigschmid and co-workers observed that if

heated rapidly, the salt can be volatilized without melting; and H. Arctowsky observed that the salt softens at  $260^\circ$ . H. W. B. Roozeboom's values for the m.p. of the hydrates are indicated in Fig. 575. J. M. Ordway gave  $35.5^\circ$  for the m.p. of the hexahydrate; F. A. Flückiger,  $38^\circ$ ; and H. W. B. Roozeboom,  $36.5^\circ$  for the hexahydrate,  $32.5^\circ$  for the hemiheptahydrate,  $56^\circ$  for the hemipentahydrate, and  $73.5^\circ$  for the dihydrate.

The **thermal dissociation** of ferric chloride,  $\text{Fe}_2\text{Cl}_6 \rightleftharpoons 2\text{FeCl}_3$ , has been discussed in connection with the mol. wt. of the salt. V. and C. Meyer noted that chlorine is evolved by the **thermal decomposition** of ferric chloride at a high temp.:  $\text{Fe}_2\text{Cl}_6 = 2\text{FeCl}_2 + \text{Cl}_2$ ; and W. Grünwald and V. Meyer observed that when ferric chloride is heated in an atm. of nitrogen, the residue contains the less volatile ferrous chloride. Thus, at:

	$448^\circ$	$518^\circ$	$606^\circ$	$750^\circ$	$>750^\circ$
Decomposition	0	0.100	0.125	0.333	0.3 to 0.5 per cent.

C. Friedel and J. M. Crafts said that the reaction is perceptible in an atm. of nitrogen at  $430^\circ$ ; according to P. Fireman and E. G. Portner, the decomposition,  $\text{Fe}_2\text{Cl}_6 \rightleftharpoons \text{Fe}_2\text{Cl}_4 + \text{Cl}_2$ , can be detected even at  $122^\circ$ ; and C. G. Maier added that the salt cannot be sublimed in vacuo without some decomposition. E. Stirnemann observed some decomposition of the ferric chloride always occurs when ferric chloride is held at  $400^\circ$  for any length of time; he found the partial press. of the chlorine in the sat. vapour of ferric chloride to be 0.08 to 0.12 atm. at  $500^\circ$ ; 24.1 mm. at  $291.5^\circ$ ; and 31.9 mm. at  $301.8^\circ$ , and this is less than 10 per cent. of the vap. press. of ferric chloride at the corresponding temp.

When the hexahydrate is slowly heated, P. Nicolardot observed that hydrogen chloride and steam, but no chlorine, are evolved; and at  $110^\circ$  the evolution of hydrogen chloride ceases, and there remains ferric oxychloride,  $\text{FeOCl}$ , which is stable in a dry atm. at temp. up to  $250^\circ$ . At a high temp. the oxychloride decomposes into ferric oxide and chloride and free chlorine. For the action of heat on aq. soln., *vide infra*.

M. H. Klaproth, E. L. Schubarth, F. A. C. Gren, J. Davy, H. Davy, and J. L. Gay Lussac noted the **volatility** of ferric chloride. T. Carnelley and W. C. Williams observed that the salt begins to sublime at  $100^\circ$ ; and C. Friedel and J. M. Crafts, and G. Herrmann, that it volatilizes at its m.p. W. Grünwald and V. Meyer found that the volatilization is slow at  $450^\circ$ , but rapid at  $600^\circ$ . According to K. F. Föhr, W. Skey, D. H. Browne, and A. Vogel, some ferric chloride is lost by volatilization during the evaporation of acidified soln. of the salt; but C. R. Fresenius, L. L. de Koninck, H. P. Talbot, R. W. Atkinson, and H. Seward consider that there is no appreciable loss by evaporation, even at  $130^\circ$ . H. P. Talbot observed a loss of iron when the soln. contains ammonium chloride, or aqua regia. C. Hüttner observed no loss during many hours' evaporation of a soln. on the water-bath, with repeated additions of hydrochloric acid, and a prolonged drying of the residue on the water-bath.

E. Stirnemann gave for the **vapour pressure**,  $p$  atm., of anhydrous ferric chloride at:

	253°	271°	285°	301°	310°	370°	403°	493°
$p$	0.0454	0.131	0.283	0.676	0.855	2.04	3.31	9.1 atm.
	Sublimation curve				Boiling curve			

E. Stirnemann's results are plotted in Fig. 576. The sublimation curve  $AO$ , Fig. 576, corresponds with  $\log p = 12.442 - 7250T^{-1}$ ; and the boiling curve  $OB$ , Fig. 576, with  $\log p = 4.138 - 2544T^{-1}$ . The partial press. of the chlorine in the reaction  $\text{Fe}_2\text{Cl}_6 \rightleftharpoons 2\text{FeCl}_2 + \text{Cl}_2$  is discussed above;  $OC$  represents the fusion curve, or the assumed effect of press. in the m.p. E. Baur studied the system. K. Jellinek and R. Koop gave for the vap. press.,  $p$  atm., at  $200^\circ$ ,  $240^\circ$ ,  $260^\circ$ , and  $280^\circ$ , the respective values  $p = 0.012$ ,  $0.088$ ,  $0.237$ , and  $0.508$  atm., and C. G. Maier obtained for the dissociation and vap. pressures combined,  $p$  mm.:

	216.5°	248.7°	273.4°	285.0°	299.6°	308.8°	313.3°	318.4°
$p$	3.9	26.6	92.6	162.5	340.9	564.2	729.6	872.6 mm.

W. Kangro and R. Flügge found the partial press.,  $p$  atm., of ferric chloride, and the equilibrium constant,  $K$ , when the press. of the chlorine is 1 atm., to be:

	327°	527°	727°	927°	1127°	1327°
$p$	0.00044	0.0061	0.030	0.086	1.8	3.3 atm.
$K$	$7.9 \times 10^{-24}$	$7.9 \times 10^{-16}$	$5.0 \times 10^{-11}$	$7.9 \times 10^{-9}$	$1.6 \times 10^{-3}$	$1.0 \times 10^{-3}$

According to G. Herrmann, the vap. press. of ferric chloride is strongly depressed in the presence of lead and other chlorides; as a result, the mixtures can be heated to a relatively high temp. without the sublimation of the ferric chloride.

H. Lescœur found the vap. press. of a sat. soln. of the hexahydrate is 6.5 mm. at  $20^\circ$ ; and H. W. B. Roozeboom found the vap. press. of a soln. sat. with the hexahydrate at  $15^\circ$  to be 6.0 mm. for  $BC$ , Fig. 575, and 1.4 mm. for  $CN$ , Fig. 575; for a soln. sat. with the hemiheptahydrate, 2.3 mm. for  $OD$ , Fig. 575; for a soln. sat. with the hexahydrate and the hemiheptahydrate, 1.8 mm.; and for a soln. sat. with the hemipentahydrate, 1.3 mm. for  $MF$ , Fig. 575—*vide supra*, the preparation of the hydrates. H. Lescœur measured the vap. press. of the different hydrates and found for  $\text{Fe}_2\text{Cl}_6 \cdot n\text{H}_2\text{O}$ , the vap. press.  $p$  mm., at about  $20^\circ$ :

$n$	13.1	12.35	12.0	11.9	8.45	7.45	5.23
$p$	6.5	5.6	2.8	2.2	2.0	1.2	1.2
	Hexahydrate			Hemihydrate		Hemipentahydrate	

The **boiling-point** of anhydrous ferric chloride was determined by C. Friedel and J. M. Crafts, K. Hachmeister gave  $307^\circ$  for the b.p.; and C. G. Maier computed  $315^\circ$  from the sublimation curve, and E. Stirnemann,  $317^\circ$ . C. G. Maier observed that some decomposition occurs at the b.p. E. Stirnemann calculated the **critical temperature** to be between  $650^\circ$  to  $700^\circ$ , and the **critical pressure**, 45 to 50 atm. E. Stirnemann calculated for the **heat of sublimation**, 33,100 cal. per mol.  $\text{Fe}_2\text{Cl}_6$ ; for the **heat of vaporization**, 11,300 cal. per mol.  $\text{Fe}_2\text{Cl}_6$ ; and for the **heat of fusion**, 21,800 cal. per mol. of  $\text{Fe}_2\text{Cl}_6$ ; K. Jellinek and R. Koop, 24,780 cal. per

mol.  $\text{Fe}_2\text{Cl}_6$  for the heat of vaporization ; W. Kangro and R. Flügge gave 24,000 cal. per mol.  $\text{Fe}_2\text{Cl}_6$  for the heat of vaporization ; and C. G. Maier gave for the heat of vaporization in cal. per mol. :

	256.9°	270.7°	288.2°	301.4°	309.2°	315.0°
Heat of vaporization .	29,410	30,590	32,480	34,110	35,090	35,470

T. Andrews obtained a value for the **heat of formation** of ferric chloride which J. Thomsen considered too high, and he calculated from the observations  $2\text{Fe} + 2\text{Cl}_2 + \text{Aq.} = 2\text{FeCl}_2.\text{Aq.} + 199.9$  Cals., and  $2\text{FeCl}_2.\text{Aq.} + \text{Cl}_2 = 2\text{FeCl}_3.\text{Aq.} + 55.54$  Cals. that  $2\text{Fe} + 3\text{Cl}_2 + \text{Aq.} = 2\text{FeCl}_3.\text{Aq.} + 255.44$  Cals.; and since  $2\text{FeCl}_3 + \text{Aq.} = 2\text{FeCl}_3.\text{Aq.} + 63.36$  Cals., it follows that  $2\text{Fe} + 3\text{Cl}_2 = 2\text{FeCl}_3 + 192.08$  Cals., or  $\text{Fe} + \frac{3}{2}\text{Cl}_2 = \text{FeCl}_3 + 96.04$  Cals. M. Berthelot gave 96.15 Cals.; W. Biltz and C. Fendius, 96 Cals.; and K. Jellinek and R. Koop, 96.04 Cals. J. Thomsen also gave  $(\text{FeCl}_2, \frac{1}{2}\text{Cl}_2, \text{Aq.}) = 27.8$  Cals. J. Thomsen gave  $\text{Fe} + \frac{3}{2}\text{Cl}_2 + \text{Aq.} = \text{FeCl}_3.\text{Aq.} + 127.72$  Cals., a result in good agreement with T. Andrews' value. M. Berthelot gave 127.85 Cals., and observed that the chlorination of iron in the presence of water furnishes 50 Cals. per atom of chlorine for the first two atoms, and 28 Cals. for the third atom of chlorine. J. Thomsen observed that, at 18°, the oxidation of  $0.1M\text{-FeCl}_2$  by chlorine furnishes  $2\text{FeCl}_2.\text{Aq.} + 2\text{HCl}.\text{Aq.} + \text{Cl}_2 = 2\text{FeCl}_3.\text{Aq.} + 2\text{HCl}.\text{Aq.} + 55.48$  Cals., and when hypochlorous acid, or potassium permanganate is used as oxidizing agent, the mean value is 55.542 Cals. M. Berthelot made observations on this subject; with oxygen as the oxidizing agent,  $2\text{FeCl}_2.\text{Aq.} + \frac{1}{2}\text{O}_2 + 2\text{HCl}.\text{Aq.} = 2\text{FeCl}_3.\text{Aq.} + \text{H}_2\text{O} + 45.269$  Cals. W. Kangro and R. Flügge gave for the reaction  $2\text{Fe}_2\text{O}_3 + 6\text{Cl}_2 = 4\text{FeCl}_3 + 3\text{O}_2 - 85$  Cals.; and W. A. Roth and co-workers gave  $\text{Fe}_2\text{O}_3 + 3\text{Cl}_2 = 2\text{FeCl}_3 + 30 + 7.4$  Cals. The subject was discussed by E. Rabinowitsch and E. Thilo. J. Thomsen gave  $2\text{FeCl}_3.\text{Aq.} + \text{Fe} = 3\text{FeCl}_2.\text{Aq.} + 44.41$  Cals.; and T. Andrews, 47.6 Cals. For the **heat of hydration**, P. Sabatier gave  $\text{FeCl}_3 + 6\text{H}_2\text{O}_{\text{solid}} = \text{FeCl}_3.6\text{H}_2\text{O} + 17.56$  Cals.; and  $\text{FeCl}_3.2.5\text{H}_2\text{O} + 3.5\text{H}_2\text{O}_{\text{solid}} = \text{FeCl}_3.6\text{H}_2\text{O} + 10.36$  Cals. at 20°;  $\text{FeCl}_{3\text{solid}} + 2.5\text{H}_2\text{O}_{\text{solid}} = \text{FeCl}_3.2.5\text{H}_2\text{O} + 7.2$  Cals.

T. Andrews gave 26.8 Cals. for the **heat of solution** of ferric chloride:  $\text{FeCl}_3 + \text{Aq.} = \text{FeCl}_3.\text{Aq.}$  According to J. Thomsen, this value is too low, and he obtained 31.68 Cals., and for  $\text{Fe}_2\text{Cl}_6 + 2000\text{H}_2\text{O}$  he obtained 63.4 Cals. P. Sabatier gave 42 Cals. for the heat of soln. of  $\text{Fe}_2\text{Cl}_6$  in  $24,000\text{H}_2\text{O}$  at 28°; 11.28 Cals. at 20-8° for  $\text{Fe}_2\text{Cl}_6.12\text{H}_2\text{O}$ ; and for  $\text{FeCl}_3.2.5\text{H}_2\text{O}$  in 300 to  $600\text{H}_2\text{O}$ , 21 Cals. at 20°. W. A. Roth and co-workers gave 12.81 Cals. for the heat of soln. of crystals of ferric chloride at 97°. G. Lemoine obtained for the heat of soln. of a mol of  $\text{FeCl}_3$  in  $n$  c.c. of water, in about 5000 c.c. of hydrochloric acid, at room temp. :

$n$ . . . . .	4990	1000	333.3	250
$Q$ . . . . .	30.97	28.6	23.4	22.6 Cals.

or of a mol of  $\text{FeCl}_3$  in about 5000 c.c. of hydrochloric acid, at room temp. :

HCl . . . . .	0	0.5N-	N-	3N-	6N-
$Q$ . . . . .	30.97	31.12	29.80	29.23	24.92 Cals.

H. W. B. Roozeboom said that the heat of soln. of the hexahydrate in an aq. soln. of ferric chloride is dependent on the conc. of the ferric chloride. The process of solution is exothermal for dil. soln. with over about 40 mols of  $\text{H}_2\text{O}$  per mol of  $\text{FeCl}_3$ , and endothermal for more conc. soln. Similarly with soln. of the hemi-heptahydrate, the process is exothermal for soln. with more than about 6.5 mols of  $\text{H}_2\text{O}$  per mol of  $\text{FeCl}_3$ , and endothermal for conc. soln.; and for soln. of the hemipentahydrate the process is exothermal for dil. soln. with over about 5 mols  $\text{H}_2\text{O}$  per mol of  $\text{FeCl}_3$ , and endothermal for more conc. soln. G. Lemoine found for the **heat of dilution**,  $Q$  Cals. per mol of  $\text{FeCl}_3$  in  $m$  c.c. of soln., with  $n$  c.c. of water, between 12° and 14° :

$m$ . . . . .	250.0	333.3	1000	2000	3000
$n$ . . . . .	750.0	666.7	1000	2000	5000
$Q$ . . . . .	6.0	5.2	1.52	0.98	2.42

The greatest evolution of heat occurred with  $M$ - and  $3M$ -soln.; and no heat was evolved with a  $0.25M$ -soln.; but when a  $3M$ -soln. is diluted to  $0.25M$ -, the heat evolved is 7.7 Cals. greater than the heat of soln. of the hexahydrate, and this is attributed to a change in the state of aggregation of the water of crystallization. When a soln. with 4 gram-atoms of iron per litre is diluted with water, there is a considerable evolution of heat, which is not due to hydration because it is observed when a soln. with  $\text{Fe}_2\text{Cl}_6 + 108\text{H}_2\text{O}$  is diluted. Rather is the development of heat due to the gradual hydrolysis of the ferric chloride with the formation of hydrochloric acid, and soluble hydrated ferric oxide. The development of heat is less marked with soln. of other ferric salts. If  $M$  represents the molar conc. of a soln. of ferric chloride, the percentage changes (hydrolysis) for different dilutions are:

$M$	4	3	1.5	1.0	0.5	0.25	0.10
Change	100	74	50	46	37	35	29

F. L. Browne and J. H. Mathews found the heat of dilution,  $Q$  cal. per gram-equivalent of  $\text{FeCl}_3$ , of aq. soln. of ferric chloride:

$\text{FeCl}_3$	1.029N-	0.515N-	0.257N-	0.129N-
$Q$	190.3	1000.8	31	-38
$\text{FeCl}_3$	0.064N-	0.032N-	0.016N-	0.008N-
$Q$	-116	-191	-192	-90

The results are plotted in Fig. 577. There is first a rapid evolution or absorption of heat (depending on the conc. of the soln.) with dilution, and thereafter a slow evolution of heat which occupies many hours. This is taken to mean that the hydrolysis takes place in two stages: the first stage is rapid, the second is a slow reaction. F. L. Browne measured the heat of dilution,  $Q$  cal. per gram-equivalent of  $\text{FeCl}_3$ , and also the hydrolysis in soln. containing the following proportions of ferric chloride, expressed to show the conc. of hydrochloric acid, and of unchanged  $\text{FeCl}_3$ . All concentrations are expressed in gram-equivalents per litre:

Total $\text{FeCl}_3$	0.250	0.125	0.0625	0.0313N-
HCl	0.080	0.035	0.0173	0.0091N-
Unchanged $\text{FeCl}_3$	0.190	0.090	0.0452	0.0222N-
$Q$	31	-89	-172	-212

E. Petersen pointed out that in diluting a rather more than  $N$ - $\text{FeCl}_3$ , with  $N$ -HCl, there is an evolution of heat owing to the heat of dilution of the acid; after making an allowance for this, the heat of dilution of the soln. is negative. J. Thomsen measured the **heat of neutralization** of ferric hydroxide with hydrochloric acid, and obtained  $Q$  cal. per mol of  $\text{Fe}(\text{OH})_3$ , with:

Mols HCl	1	1.5	2	3
$Q$	5944	8766	11,504	16,728 cal.

G. Lemoine added that the heat of neutralization is dependent on the concentration and is in accord with the fact that the heat of dilution of conc. soln. of ferric chloride is less than it is with dil. soln. M. Berthelot gave  $(\text{Fe}_2\text{O}_3\text{ppd.}, 6\text{HCl.Aq.}) = 33.2$  Cals. P. Nicolardot measured the heat of neutralization of different forms of ferric oxide with hydrochloric acid.

H. Becquerel measured the **index of refraction**,  $\mu$ , of aq. soln. of ferric chloride and found for the  $D$ -line and the red  $Li$ -line, at  $15^\circ$  to  $18^\circ$  except in the case of the 70.6 per cent. soln. where the temp. was  $30^\circ$  to  $35^\circ$ , and the 75 per cent. soln. where the temp. was high enough to prevent the deposition of crystals:

$\text{FeCl}_3$	75	70.6	60	33	16.5	8.25	4.13	2.06
$\mu_{D-}$	1.6163	1.5964	1.5605	1.4382	1.3853	1.3594	1.3466	1.3403
$\mu_{Li-}$	1.6011	1.5823	1.5493	1.4332	—	—	—	—

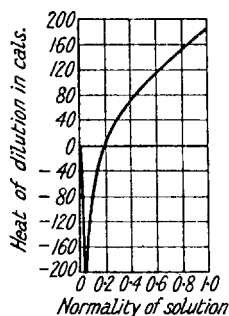


FIG. 577.—Heats of Dilution of Solutions of Ferric Chloride.



The value for water is 1.3340 with the *D*-line. G. Limann obtained with soln. of concentration *N* equivalents per litre at 18° :

<i>N</i>	0	0.5	1.0	2.0	4.0
$\mu$ { <i>H<math>\alpha</math></i> -line	1.33139	1.33859	1.34560	1.35903	1.38512
<i>D</i> -line	1.33322	1.34055	1.34769	1.36138	1.38805
<i>H<math>\beta</math></i> -line	1.33737	1.34502	1.35249	1.36698	—

Observations were also made by A. Hauke, A. Heydweiller, L. R. Ingersoll, H. C. Jones, and H. C. Jones and F. H. Getman. C. E. Richards and R. W. Roberts gave for light of wave-length,  $\lambda$ , at 17° :

$\lambda$	6104	5780	5330	5218	5150	4958
$\mu$ { 1.045 sp. gr.	1.3470	1.3484	1.3500	1.3508	1.3514	1.3535
1.167 sp. gr.	1.3904	1.3916	1.3940	1.3959	1.3969	—

H. M. Vernon discussed the change of colour which occurs on diluting or raising the temp. of the soln. The **molecular refraction** was measured by J. H. Gladstone who gave for a 27.95 per cent. soln. 50.75 for the *A*-line, and 52.64 for the *D*-line. J. H. Gladstone and W. Hibbert gave for soln. with 11.87 to 27.67 per cent. of  $\text{FeCl}_3$  in ethyl acetate the mean mol. refraction 50.36 for the *D*-line. Measurements were also made by A. Hauke. A. Heydweiller gave for soln. of concentration *C*, where *C* represents soln. with 0 to 4.0 gram-equivalents per litre, a mean value of 29.97; and G. Limann, 30.02. J. H. Gladstone and W. Hibbert, unlike A. Heydweiller, found that the result depended on the concentration, and increased with concentration at first slowly and then rapidly. A. Hauke also observed that the result depended on the concentration. G. Limann discussed the relation between the index of refraction and the electrical conductivity of the soln. He also found for the **dispersion** at 18°,  $(\mu_D - \mu_A)/C = 26.6$ , and  $(\mu_B - \mu_D)/C = 67.2$ . A. Heydweiller also studied the optical dispersion of the soln. Observations on the optical properties of soln. in methyl alcohol were made by H. C. Jones and J. A. Anderson. Those of soln. in ethyl alcohol were examined by J. Malsch, J. M. Hiebendaal, E. Schaer, J. S. Anderson, J. H. Gladstone and W. Hibbert, F. G. Donnan and H. Bassett, G. Pellini and D. Meneghini, H. C. Jones and J. A. Anderson; of soln. in ether, by K. A. Hofmann and K. Ott, K. Ott, and W. J. Russell and W. J. Orsman; of soln. in acetone, by H. C. Jones and J. A. Anderson.

G. J. Elias observed that a half sat. soln. of ferric chloride exhibits no **magnetic birefringence**—*vide supra*, the hydrosol of ferric oxide. Like soln. of the other ferric salts, ferric chloride soln. show a negative **magnetic rotatory power**, and since water exerts a positive influence, the magnetic rotation of the plane of polarization of the soln. is only a little greater than the value for water. H. Becquerel observed the magnetic rotatory power,  $\omega$ , referred to water unity, at 15° to 18° for soln. with less than 71 per cent. of  $\text{FeCl}_3$ , and at a higher temp. for more conc. soln. in order to prevent the deposition of crystals :

$\text{FeCl}_3$	80	70.58	60.5	50 per cent.
$\omega$	-23.11	-19.07	-15.584	-8.768
$\text{FeCl}_3$	33	16.5	8.25	2.06 per cent.
$\omega$	-2.674	-0.116	+0.621	+0.936

The negative values increase at a faster rate than is proportional to the increase in the conc. of the soln., and the mol. magnetic rotation which with most substances is a constant, increases with increasing concentration; only in dil. soln. is the magnetic rotatory power constant. Observations were made by H. E. J. G. du Bois, G. Quincke, P. K. Pillai, E. Miescher, O. Schönrock, W. Stscheglaieff, and M. E. Verdet. C. E. Richards and R. W. Roberts gave, at 20° :

$\lambda$	6104	5780	5330	5105	4958
$\omega$ { 1.045 sp. gr.	0.0105	0.0117	0.0135	0.0145	0.0154
1.167 sp. gr.	-0.0009	-0.0019	-0.0050	-0.0099	—

The magnetic rotation changes from positive to negative with increasing concentration of the soln.; and with a soln. of sp. gr. 1.092, the rotatory dispersion curve changes markedly near  $0.57\mu$ —probably owing to a partial dehydration of the molecule of hydrated ferric chloride. The magnetic absorptions of ferric chloride and sulphate are the same.

L. R. Ingersoll studied **Kerr's effect**, and gave for **Verdet's constant**, in a magnetic field of 12,050 gauss, with soln. of 6.3 and 47.8 per cent.  $\text{FeCl}_3$ , 0.061 and  $-0.0399$  for  $\lambda=8,000$ ; 0.0040 and  $-0.0215$  for  $\lambda=10,000$ ; and 0.0026 and  $-0.0110$  for  $\lambda=12,500$ . The value of Verdet's constant was found by M. E. Verdet, and H. E. J. G. du Bois, to be unaffected by variations in the strength of the magnetic field up to 2400 gauss; and the latter was unable to confirm W. Stscheglaieff's observation that there is a considerable deviation with fields ranging from 9000 to 16,000 gauss. L. R. Ingersoll observed that Verdet's constant varies proportionally with the third power of the wave-length over the range  $\lambda=7000$  to 13,500 Å. Observations on soln. in methyl alcohol were made by M. E. Verdet, G. Quincke, O. Schönrock, H. E. J. G. du Bois; in ether, by M. E. Verdet, and O. Schönrock. P. K. Pillai, and F. Allison and E. J. Murphy studied the magneto-optic properties of ferric chloride.

O. Stelling and F. Olsson studied the X-ray spectrum. A. E. Garrett found that ferric chloride at  $355^\circ$  emits in air **positive and negative ions**, which make the ambient air a conductor. O. W. Richardson suggested that the positive ions may be referred to the contamination of the chloride with potassium salts. The emission of positive ions by the salt was also discussed by O. Gossmann, H. Queren-gässer, G. C. Schmidt, and H. Geiger and K. Scheel, and the Becquerel effect, by J. Lifschitz and S. B. Hooghoudt. A. L. Hughes observed that ferric chloride exhibits a very feeble **photoelectric effect**, which, according to G. Dima, is smaller than is the case with ferrous chloride; and A. Pochettino, similarly with Hallwachs' effect. W. Zimmermann observed no perceptible photoelectric effect with aq. soln. of ferric chloride. M. Schneider discussed the photochemical reduction of ferric chloride. E. P. Perman showed that a little of the chloride is reduced by exposure to **canal rays** in air or in hydrogen; whilst K. Niederstadt found that **radium rays** are without action. For the decomposition in light, *vide infra*.

E. N. da C. Andrade found that a flame is coloured yellow by ferric chloride, and that the **flame spectrum** has bands in the red, green, and yellow. R. Zsigmondy showed that unlike soln. of ferrous chloride, the transparency of soln. of ferric chloride for **heat rays** is only a little smaller than is the case with water. J. S. Anderson observed that the mol. extinction coeff.,  $k$ , of soln. of ferric chloride, containing  $C$  mols of  $\text{FeCl}_3$  per litre, for ultra-red rays of wave-lengths,  $\lambda$ , are:

$\lambda$	7100	7880	8370	9000	9680	10,620	11,750 Å.
$k_{c=2.0}$	0.08	0.09	0.11	0.12	0.10	0.06	0.03
$k_{c=0.2}$	0.16	0.25	0.23	0.20	0.14	0.06	—

No change with ageing was observed. T. Dreisch observed a band with a maximum at 8300 Å. Not a tenth part of the energy is absorbed at the maximum that is absorbed in the maximum of the ferrous sulphate band. According to J. Königs-berger and K. Küpferer, the **absorption spectrum** of the yellowish-red vapour of ferric chloride, at  $250^\circ$ , has a band in the blue and violet; and C. Sheard and C. S. Morris found a continuous band between 5900 Å. and 4800 Å. in the emission spectrum of ferric chloride. F. I. G. Rawlins and C. P. Snow found in the anhydrous crystals, an absorption band about 5000 Å., and one about 6200 Å. V. L. Bohnson and A. C. Robertson observed no bands in the absorption spectrum of aq. soln. of ferric chloride; H. C. Jones and J. A. Anderson said that the soln. are almost transparent for the whole of the visible spectrum; and B. E. Moore found that there is a sharp absorption band at the short-wave end with conc. soln., but with dil. soln. the edges of the band are not so clear. From the records of A. Byk and H. Jaffe, H. C. Jones and J. A. Anderson, S. M. Karim and R. Samuel, and G. P. Drossbach, it follows that the position of the absorption

band varies with the conc. of the soln. C. Lepière recommended a conc. soln. of chromic acid and ferric chloride to remove the orange rays. Observations on the absorption spectrum, and the mol. extinction coeff. were made by J. von Koczkas, G. Lemoine, T. Ewan, and R. A. Houston and C. Cochrane; V. L. Bohnson and A. C. Robertson's results are summarized in Fig. 559—*vide* the ferrates. J. S. Anderson gave for soln. with  $C$  mols of  $\text{FeCl}_3$  per litre :

$\lambda$ . . .	7170	6870	6530	5820	5290	4990	4340 A.
$k$ { $C=2.0$ . . .	0.08	0.09	0.11	0.17	0.9	5.7	—
$C=0.2$ . . .	—	0.12	0.10	0.21	1.0	2.15	18.6

The effect of hydrolysis is shown by observations on freshly prepared soln., and on soln. aged 6 weeks, for  $\lambda=5290$  A. :

$C$ . . .	4	3	2	1.4	0.8	0.2	0.02
$k$ { Fresh . . .	3.43	1.77	0.86	0.63	0.63	0.84	1.75
Aged . . .	2.37	1.26	0.63	0.51	0.52	0.81	0.75

G. Lemoine showed that Beer's rule applies approximately for conc. soln., but with decreasing concentration the rule fails. J. von Koczkas also noted the failure of Beer's law and of Lambert's law with soln. of ferric chloride owing to hydrolysis. B. E. Moore attributes the failure to the breaking down with dilution of strongly absorbent complexes into feebly absorbent ions. There are also disturbances due to the formation of intensely coloured, colloidal complexes by the hydrolysis of the aq. soln. Beer's rule also applies better for light of long wave-length than for light of short wave-length. The subject was also discussed by J. S. Anderson, U. Antony and G. Giglio, T. Ewan, H. C. Jones and J. A. Anderson, A. Müller, and S. U. Pickering. W. J. Russell and W. J. Orsman found that a soln. of ferric chloride sat. with hydrogen chloride has an absorption spectrum with bands extending to 7180, from 7000 to 6800, from 6620 to 6510, from 6310 to 6200, from 6030 to 5920, from 5500 to 5200, 5110 to 4970, and from about 4830 to about 4500. Excepting for the bands 6030 to 5920, and 5110 to 4970, the spectrum is similar to that observed with cobaltous chloride similarly treated. Similar remarks apply to ethereal soln. sat. with hydrogen chloride. H. C. Jones and J. A. Anderson observed that additions of calcium or aluminium chloride act somewhat similarly. Observations were also made by A. Byk and H. Jaffe, and G. Lemoine. O. Gossmann studied the emission of positive ions by heated ferric chloride; and A. Pochettino, the Hallwach's effect.

H. Querengässer measured the **electrical conductivity** of the vapour of ferric chloride—*vide supra*. According to W. Hampe, ferric chloride dissociates on heating to form some ferrous chloride, and it is therefore electrically conducting; but a soln. of dry ferric chloride in dry ether does not conduct. If a trace of moisture be present, the soln. is a conductor, and hydrogen is evolved at the negative pole, but no gas comes off from the positive pole; with more water, iron is deposited, but although hydrogen is evolved no ferrous chloride forms, as otherwise, owing to its insolubility in ether, it would be deposited on the negative pole, which is not the case. No chlorine is evolved, as it enters into secondary combination. Ferric chloride is therefore not an electrolyte, but when mixed with water it becomes one. This conversion is attributed to the formation of a compound,  $\text{Fe}_2\cdot\text{Cl}_6\text{H}_6\cdot\text{O}_6\text{H}_6$ , corresponding to the compound supposed to be formed with hydrochloric acid and water. Electrolysis would break it up into the groups  $2\text{Fe}^{\dots}$  and  $6(\text{ClH}\cdot\text{OH})$ , which would fully explain the occurrence of many secondary reactions. Measurements of the electrical conductivity of aq. soln. were made by C. Cattaneo, and E. Wertyporoch and I. Kowalsky; and H. M. Goodwin gave for the eq. conductivity,  $\lambda$  of soln. with one eq. of ferric chloride in  $v$  litres of water, at  $25^\circ$  :

$v$ . . .	9.90	19.80	39.6	79.2	158.4	316.8	633.6
$\lambda$ . . .	81.5	96.7	113.0	130.3	148.3	166.3	181.8

R. Peters obtained analogous results. H. Mosler's values for the sp. conductivity

of soln. of ferric chloride are summarized in Fig. 578. The dotted line refers to the temp. coeff.,  $\alpha$ , of the conductivity. The conductivity increases to a maximum, with approximately  $M\text{-FeCl}_3$ , and it then decreases; the maximum is the more pronounced the higher is the temp. Observations were also recorded by H. C. Jones and co-workers, H. M. Goodwin and F. W. Grover, and A. Heydweiller. E. Moles and co-workers gave for the mol. conductivity,  $\mu$ , mhos, of soln. with  $C$  mols of the salt in a litre. Similarly also for the temp. coeff.,  $\alpha$ , of the conductivity:

$C$		0.0507	0.2009	0.7379	1.4758	2.9515	3.9370
$\mu$	$0^\circ$	163	120.3	70.0	36.15	8.42	3.0
	$18^\circ$	268.3	190.8	108.5	—	15.33	6.11
	$25^\circ$	312.63	219.8	128.3	65.39	18.42	7.59
	$35^\circ$	381.1	262.6	145.6	77.91	23.08	—
$\alpha$	$0^\circ$ to $18^\circ$	2.71	2.52	2.40	2.42	3.23	3.70
	$18^\circ$ to $25^\circ$	2.18	2.02	1.83	1.79	2.61	3.08
	$25^\circ$ to $35^\circ$	1.98	1.81	1.62	1.75	2.19	—

The limiting value for the mol. conductivity of non-hydrolyzed ferric chloride at  $25^\circ$  for infinite dilution was found by N. Bjerrum to be  $\mu_\infty = 435$ ; and the limiting value for the eq. conductivity at  $18^\circ$  was found by A. Heydweiller, and G. Limann to be  $\lambda_\infty = 126.5$ . E. Moles and co-workers showed that the temp. coeff. decreases with increasing concentration to a minimum, and then increases—*vide* Fig. 578—and the position of the minimum corresponds with the maximum in the conductivity curve. The effect of temp. on the conductivity was also measured by C. Cattaneo, H. C. Jones and co-workers, G. Malfitano and L. Michel, G. Malfitano, and H. Mosler. J. A. Fleming and J. Dewar observed that by cooling the soln. to  $-198^\circ$ , it is almost completely non-conducting, for the resistance is 10,000 megohms at  $-198^\circ$ , and nearly the same at  $-156^\circ$ , and there is then an abrupt change, for it becomes 0.2 megohm at  $-115^\circ$ . G. Berndt found that the effect of a magnetic field of 3000 gauss is less than 0.004 per cent. of the value of the conductivity.

H. C. Jones and C. M. Stine measured the effect of mixed soln. of aluminium and ferric chlorides. L. Kahlenberg and co-workers found the mol. conductivity,  $\mu$ , of soln. of a mol of ferric chloride in  $v$  litres of solvent, at  $25^\circ$ , to be:

Methyl alcohol	$v$	3.20	12.81	51.24	204.96	819.83	1639.66
	$\mu$	20.81	31.09	49.00	172.61	111.08	147.08
Ethyl alcohol	$v$	2.89	11.57	23.14	92.56	195.1	390.2
	$\mu$	9.91	13.70	14.50	16.7	19.33	21.20
Acetone	$v$	14.65	58.60	117.19	234.39	937.54	1875.1
	$\mu$	51.70	64.65	68.68	70.67	83.76	91.22
Ethyl acetate	$v$	16.89	33.78	67.46	—	—	—
	$\mu$	0.87	1.12	1.25	—	—	—
Ethyl acetoacetate	$v$	5.46	22.14	31.90	157.98	240.51	543.06
	$\mu$	10.82	14.62	15.25	19.79	20.65	23.43
Benzaldehyde	$v$	25.58	51.65	117.91	157.79	237.14	—
	$\mu$	14.32	14.58	13.05	12.14	10.50	—
Nitrobenzene	$v$	2.84	11.34	45.4	181.5	726	2903.9
	$\mu$	3.76	6.58	16.25	18.86	20.51	20.45
Hydrogen cyanide	$v$	4.2	22.9	431.1	1042.0	—	—
	$\mu$	111.7	152.4	231.7	259.9	—	—
Amylamine	$v$	5.0	13.4	27.1	—	—	—
	$\mu$	0.22	0.16	0.09	—	—	—

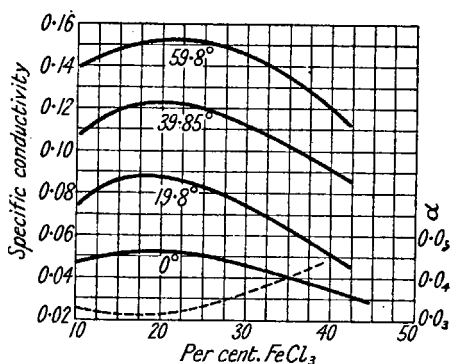


FIG. 578.—The Specific Electrical Conductivity of Solutions of Ferric Chloride.

The effect at a temp. of  $\theta^\circ$ , is for ethyl acetoacetate with  $v=5.49$  at  $25^\circ$ ,

Ethyl	{	$\theta$	.	.	.	$25^\circ$	$50^\circ$	$60^\circ$	$70^\circ$	$86^\circ$	$100^\circ$
acetoacetate		$\mu$	.	.	.	12.0	16.8	18.2	19.9	21.7	21.7
Benzaldehyde	{	$\theta$	.	.	.	$25^\circ$	$52^\circ$	$80^\circ$	$90^\circ$	$105^\circ$	$125^\circ$
		$\mu$	.	.	.	14.3	20.5	25.9	26.4	24.1	24.0
Nitrobenzene	{	$\theta$	.	.	.	$25^\circ$	$67^\circ$	$85^\circ$	$110^\circ$	$135^\circ$	$150^\circ$
		$\mu$	.	.	.	5.2	8.8	11.0	14.6	16.7	16.9

Observations with methyl alcohol were also made by H. C. Jones and C. F. Lindsay, and L. I. Shaw; on ethyl alcohol, by A. T. Lincoln, and C. Cattaneo; A. T. Lincoln found for allyl alcohol for  $v=22.02$ ,  $53.71$ , and  $115.6$  at  $25^\circ$ ,  $\mu=17.42$ ,  $23.03$ , and  $32.5$  respectively; and for  $v=20.02$  at  $25^\circ$ ,  $50^\circ$ ,  $73^\circ$ , and  $80^\circ$ ,  $\mu=17.42$ ,  $34.62$ ,  $43.63$ , and  $45.63$  respectively; L. Kahlenberg and A. T. Lincoln, and A. T. Lincoln gave for soln. in benzyl alcohol for  $v=88.06$  and  $895.22$  at  $25^\circ$ ,  $\mu=2.62$  and  $6.31$  respectively; and for  $v=88.06$ , at  $25^\circ$ ,  $54^\circ$ ,  $85^\circ$ , and  $100^\circ$ ,  $\mu=2.62$ ,  $5.08$ ,  $6.46$ , and  $7.19$  respectively; L. Kahlenberg and A. T. Lincoln found soln. in glycol are good conductors; and for the sp. conductivity,  $\kappa$  mho, of soln. of  $C$  mol of  $\text{FeCl}_3$  per litre, they gave for  $C=0.000339$  at  $0^\circ$ ,  $2.8^\circ$ , and  $24.1^\circ$ ,  $\kappa \times 10^9=0.0108$ ,  $0.0115$ , and  $0.0708$  respectively; for  $C=0.00431$  at  $0^\circ$ ,  $10.8^\circ$ , and  $21.6^\circ$ ,  $\kappa \times 10^9=0.132$ ,  $0.339$ , and  $0.722$  respectively; and for  $C=0.0337$  at  $0^\circ$ ,  $13.0^\circ$ , and  $23.1^\circ$ ,  $\kappa \times 10^9=0.512$ ,  $1.44$ , and  $3.11$  respectively. Observations on the conductivity of soln. in glycerol were also made by C. Cattaneo, and J. Timmermans. W. Hampe, and L. Kahlenberg and A. T. Lincoln said that a soln. of dry ferric chloride in dry ether is non-conducting, but C. Cattaneo found that the sp. conductivities of soln. of  $0.0407$ ,  $0.0079$ , and  $0.0042$  mols  $\text{FeCl}_3$  per litre are respectively  $0.550$ ,  $0.068$ , and  $0.0377$  mho. The temp. coeff. is negative between  $10^\circ$  and  $30^\circ$ . J. Timmermans also studied the mol. conductivity; and H. E. Williams, the electrolysis of wet ethereal soln. L. Kahlenberg and A. T. Lincoln, L. Kahlenberg, and A. T. Lincoln found that soln. of a mol of ferric chloride in  $v=4.37$ ,  $21.32$ ,  $81.88$ , and  $575.50$  litres of paraldehyde at  $25^\circ$  has the respective mol. conductivities  $\mu=9.81$ ,  $16.91$ ,  $19.16$ , and  $16.91$ ; with soln. in salicylaldehyde,  $v=20.39$ ,  $81.38$ , and  $220.74$  when  $\mu=3.76$ ,  $4.71$  and  $5.60$  respectively; with furfural,  $v=45.60$ ,  $80.98$ , and  $149.21$  when  $\mu=20.78$ ,  $22.20$ , and  $26.42$  respectively; in the soln. in methylpropylketone,  $v=13.64$ ,  $100.71$ , and  $1074.27$  when  $\mu=28.25$ ,  $42.75$ , and  $59.52$  respectively; with soln. in acetophenone, when  $v=23.46$ ,  $65.77$ , and  $292.98$ , then  $\mu=10.28$ ,  $11.59$ , and  $13.08$  respectively; with soln. in amyl nitrite, when  $v=21.34$ ,  $69.46$ , and  $644.56$ ,  $\mu=1.54$ ,  $2.02$ , and  $3.73$  respectively; with soln. in methyl thiocyanate, when  $v=2.321$ ,  $18.15$ , and  $24.68$ ,  $\mu=27.20$ ,  $39.63$ , and  $42.52$  respectively; with soln. in ethyl thiocyanate, for  $v=1.1146$ ,  $8.865$ , and  $5.37$ ,  $\mu=15.96$ ,  $32.44$ , and  $42.43$  respectively; with amyl thiocyanate, when  $v=2.935$ ,  $15.77$ , and  $193.5$ ,  $\mu=8.32$ ,  $13.06$ , and  $23.52$  respectively; with ethyl isothiocyanate, when  $v=3.039$ ,  $6.793$ , and  $26.10$ ,  $\mu=10.68$ ,  $12.18$ , and  $11.59$  respectively; with ethyl monochloroacetate, with  $v=7.76$ ,  $45.63$ , and  $152.55$ ,  $\mu=12.45$ ,  $14.78$ , and  $17.88$  respectively; with ethyl cyanoacetate, with  $v=15.30$ ,  $44.64$ , and  $185.22$ ,  $\mu=8.88$ ,  $9.80$ , and  $11.57$  respectively; with diethyl oxalate, when  $v=13.15$ ,  $42.29$ , and  $342.85$ ,  $\mu=5.88$ ,  $5.92$ , and  $7.70$  respectively; with ethyl benzoate, when  $v=20.54$ ,  $174.28$ , and  $517.21$ ,  $\mu=1.55$ ,  $1.61$ , and  $1.91$  respectively; with *m*-nitrotoluene, when  $v=10.86$ ,  $84.77$ , and  $814.8$ ,  $\mu=6.86$ ,  $12.55$ , and  $18.20$  respectively; with *o*-nitrotoluene, when  $v=10.94$ ,  $74.28$ , and  $201.4$ ,  $\mu=8.37$ ,  $13.32$ , and  $15.24$  respectively; with pyridine, when  $v=6.06$ ,  $24.56$ , and  $95.35$ ,  $\mu=7.96$ ,  $6.85$ , and  $6.41$  respectively; and L. Kahlenberg and O. E. Ruhoff found that with amylamine, when  $v=5.021$ ,  $18.34$ , and  $27.05$ ,  $\mu=0.217$ ,  $0.138$ , and  $0.086$  respectively. A. P. Julien measured the conductivity of soln. in selenium oxychloride; and E. Wertyporoch and I. Kowalsky, in various non-aqueous solvents.

When an aq. soln. of ferric chloride is evaporated, hydrochloric acid is evolved, and hydrated ferric oxide or oxychloride is deposited; H. W. B. Roozeboom observed that when the aq. soln. is evaporated on a water-bath, it cannot be

concentrated much farther than  $\text{FeCl}_3 \cdot 2.5\text{H}_2\text{O}$ . The **hydrolysis** is represented by the equation:  $\text{FeCl}_3 + 3\text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})_3 + 3\text{HCl}$ ; and, according to E. Stirnemann, this reaction occurs at temp. below  $200^\circ$ , or at the most  $350^\circ$ , but at higher temp. reactions represented by  $\text{FeCl}_3 + \text{H}_2\text{O} = \text{FeOCl} + 2\text{HCl}$ , and  $2\text{FeCl}_3 + 3\text{H}_2\text{O} = \text{Fe}_2\text{O}_3 + 6\text{HCl}$  may occur. According to F. W. C. Krecke, all aq. soln. of ferric chloride are hydrolyzed when heated, and this the more the higher the temp. Soln. with over 4 per cent. of ferric chloride can be heated to  $100^\circ$  without decomposition, but in a sealed vessel, at a higher temp., more or less complete hydrolysis occurs. As the soln. becomes darker in colour, T. Graham's soluble hydrated ferric oxide is formed, and it is precipitated by alkali salts; and if the soln. with 4 to 32 per cent. of ferric chloride is not heated above  $100^\circ$ , the hydrolysis which occurs is reversed as the soln. cools, and with soln. having 1 to 4 per cent. ferric chloride, the re-combination of the products proceeds slowly as the soln. is cooled, but if the soln. has less than 1 per cent. of ferric chloride, re-combination of the products of hydrolysis does not occur as the soln. cools. If the soln. with over 1 per cent. of ferric chloride be heated for a long time, or heated to a higher temp., an insoluble oxychloride is precipitated, and this goes into compact, black, anhydrous, ferric oxide. If the soln. with less than 1 per cent. of ferric chloride be heated for a long time, L. P. de St. Gilles' sparingly soluble hydrated oxide is formed, and this makes the soln. turbid. These results are summarized in Table XCI.

TABLE XCI.—THE ACTION OF HEAT ON AQUEOUS SOLUTIONS OF FERRIC CHLORIDE.

$\text{Fe}_2\text{Cl}_6$ per cent.	T. Graham's soluble hydrated ferric oxide	L. P. de St. Gilles' hydrated ferric oxide	Oxychloride	Ferric oxide
32	at $100^\circ$ – $130^\circ$	—	$< 100^\circ$	$140^\circ$
16	$100^\circ$ – $120^\circ$	—	$< 100^\circ$	$120^\circ$
8	$100^\circ$ – $110^\circ$	—	$< 100^\circ$	$110^\circ$
4	$90^\circ$ – $100^\circ$	—	$90^\circ$	—
2	$87^\circ$	—	$87^\circ$	—
1	$83^\circ$	$100^\circ$ – $130^\circ$	—	—
0.5	$75^\circ$	$100^\circ$ – $130^\circ$	—	—
0.25	$64^\circ$	$100^\circ$ – $130^\circ$	—	—
0.125	$54^\circ$	$100^\circ$ – $130^\circ$	—	—
0.0625	$36^\circ$	$100^\circ$ – $130^\circ$	—	—

Observations on the hydrolysis and ageing of ferric chloride in aq. soln. were made by R. Phillips, H. de Sénarmont, J. M. Ordway, N. N. Petin and co-workers, L. Liechti and W. Suida, Z. H. Skraup and co-workers, R. Haller, E. Lesche, N. Sahlbom, G. Jander and W. Scheele, E. Erlenmeyer, M. Gieseler, M. Goble, B. Sandrock, A. Tian, K. Schuwirth, J. Attfield, B. de Buisson, G. C. Wittstein, C. R. Fresenius, H. Ditz, H. M. Vernon, C. R. C. Tichborne, A. Vogel, W. Bachmann, F. W. C. Krecke, and D. Tommasi.

W. Spring noted that **Tyndall's optical test**—1. 13, 7—shows that dil. aq. soln. are not optically empty, even though in diffuse daylight they seem quite clear. The Tyndall effect is lessened by the addition of dil. hydrochloric acid, and it disappears if conc. hydrochloric acid be added. D. Vorländer, and W. Bachmann found with the ultramicroscope that the soln. are almost free from colloidal particles, but with a dilution of  $0.0005N\text{-FeCl}_3$ , and using polarized light, a discontinuity can be detected. This is due to the presence of colloidal ferric hydroxide. These particles appear larger if sodium chloride be added, and disappear if hydrochloric acid is added. E. Lesche observed that during the ageing of the soln. the particles dehydrate and become increasingly lyophobic—the change is irreversible.

The change which occurs in the electrical conductivity of dil. aq. soln. of ferric chloride by ageing was attributed by G. Vicentini to hydrolysis, and this was confirmed by G. Foussereau, E. Puxeddu, etc. U. Antony and G. Giglio observed

that whilst a freshly-prepared soln. with less than 1.1 per cent. of ferric chloride, is colourless when viewed in a 40-cm. tube, it acquires a yellow colour on standing for some hours, and the colour becomes deeper 48 hrs. after the soln. has been prepared. Soln. with less than 0.00083 per cent. of  $\text{FeCl}_3$  show no coloration with potassium ferrocyanide. The facts are here explained by assuming that in aq. soln., ferric chloride is hydrolyzed:  $\text{FeCl}_3 + 3\text{H}_2\text{O} = 3\text{HCl} + \text{Fe}(\text{OH})_3$ . L. Vanzetti illustrated the hydrolysis by filling a tube about three-quarters of its length with a hot, 5 to 10 per cent. soln. of gelatin rendered faintly pink by a trace of alkali and phenolphthalein. When the gelatin has "set," a 10 per cent. soln. of ferric chloride is added. As diffusion proceeds, two layers appear: (i) The lower colourless layer is due to the more rapid diffusion of the hydrochloric acid produced by the hydrolysis, and (ii) an upper, more or less opaque layer of brown hydrated ferric oxide. E. Moles and co-workers found that the conductivity of 0.1M- $\text{FeCl}_3$  remained constant for about a month, but A. Quartaroli observed that a 0.07M-soln., at 25°, increased about 3.5 per cent. during 1 month, and 3.9 per cent. during 3 months. H. M. Goodwin found that when a neutral soln. of ferric chloride

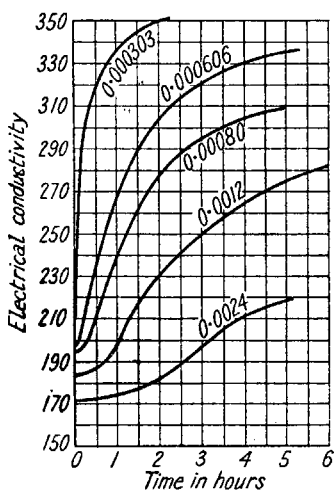


FIG. 579.—The Effect of Time on the Electrical Conductivity of Solutions of Ferric Chloride.

is progressively diluted, the soln., colourless at first, soon becomes yellow, and the mol. conductivity increases at the same time. The mol. conductivity at first assumes a constant value—*quiescent period*—for dilutions ranging up to 0.001M- $\text{FeCl}_3$ , but with greater dilutions, the conductivity changes with time as illustrated in Fig. 579. The curves in this diagram show that (i) the mol. conductivity of dil. soln. increases with time; (ii) the rate of increase rapidly increases with dilution; (iii) the increase in the conductivity does not begin at once, but only after the lapse of a definite interval of time; (iv) the initial lag, or the quiescent period, increases as the conc. of the soln. increases; (v) the time required for equilibrium increases enormously with increasing concentrations; and (vi) the reaction goes slowly at first—*primary hydrolysis*—then proceeds with increasing rapidity—*secondary hydrolysis*—and afterwards slowly until equilibrium is attained. Analogous results were obtained by G. Bongiovanni, C. Cattaneo, A. Dumansky, T. C. Fitzpatrick, G. Foussereau, A. Lottermoser and E. Lesche, E. Heymann, H. C. Jones and co-workers, W. Jufereff, G. Malfitano, G. Malfitano and L. Michel, R. Peters, E. Puxeddu, A. Tian, G. Vicentini, and C. L. Wagner. The results of H. M. Goodwin and F. W. Grover are plotted in Fig. 579. When the temp. is raised the quiescent period is shortened, the period of acceleration is hastened, and the time required for equilibrium is shortened. A fall of temp. from 25° to 10° has nearly the same effect in retarding the reaction as increasing the concentration about three times; lowering the temp. to 0°, retards the reaction as much as increasing the concentration 15 to 20 times. As emphasized by G. Malfitano, and G. Malfitano and L. Michel, L. Michel, E. Heymann, B. E. Moore, etc., after the quiescent period during which no hydrolysis occurs, the hydrolysis may be assumed to occur in two stages. The first stage of the hydrolysis—or *primary hydrolysis*—is attended by a change in the properties of the soln.; for instance, the electrical conductivity increases far more than corresponds with the ionization of the ferric chloride. According to E. Heymann, the ferric ions begin to disappear, and more mobile hydrogen ions take their place. H. M. Goodwin observed that, according to the degree of dilution, the soln. are at first more or less colourless, and the colour does not change so long as the conductivity is constant. U. Antony

and G. Giglio found that a freshly-prepared 0.02 to 0.0004*M*-soln. does not redden litmus, showing that hydrolysis, recognizable by this test, has taken place; it is not rendered turbid by coagulative influence of sodium chloride; it reacts with hydrogen sulphide; and it gives a blue precipitate with potassium ferrocyanide. W. Spring found that when a current of air is passed through a soln. of greater concentration than *M*-FeCl<sub>3</sub>, some hydrogen chloride passes off, indicating that even with these soln. some hydrolysis has occurred. G. Malfitano and L. Michel showed that with very dil. soln. the increase in the primary hydrolysis produced by dilution, or by a rise of temp. can be reversed by gentle evaporation or cooling.

In the second stage of the hydrolysis—or *secondary hydrolysis*—there is a gradual change in the properties of the soln. until a state of equilibrium is attained. The rate at which the state of equilibrium is inaugurated is determined by the temp. and concentration of the soln., as well as by the presence of certain foreign substances. The duration, *t*, of the period of secondary hydrolysis was found by H. M. Goodwin, H. M. Goodwin and F. W. Grover, G. Malfitano, C. L. Wagner, and G. Fousseureau to be dependent on the concentration of the soln.; expressing the concentration, *C*, in mols of FeCl<sub>3</sub> per litre, H. M. Goodwin found that:

<i>C</i>	.	.	.	0.0006	0.0012	0.0024	0.01515
<i>t</i>	.	.	.	1 min.	15 min.	25 min.	3 days

With the most conc. soln., the time occupied by the second stage of the hydrolysis is inordinately long. According to G. Malfitano, G. Fousseureau, and E. Puxeddu, the time is also abbreviated by raising the temp. Thus, H. M. Goodwin and F. W. Grover found that with 0.00044*M*-FeCl<sub>3</sub>, the change was very rapid at 25°; it occupied 5 mins. at 15.5°; and a day at 0°; whilst with a 0.00088*M*-soln., no perceptible change was observed during 4 days at 0°. The time, *t*, required for the soln. to attain a state of equilibrium was found by H. M. Goodwin to be 3 hrs. at 25° for a 0.00010*M*-soln., and about a week for a 0.00061*M*-soln.; by H. M. Goodwin and F. W. Grover, between 8 and 24 hrs. for a 0.00005*M*-soln. at 0°, and 1.5 hrs. at 24.92°; 2 hrs. for a 0.00015*M*-soln. at 25.12°, and a day for a 0.00030*M*-soln. at 15.7°; by A. Quartaroli, 3 hrs. at 25° for a 0.00011*M*-soln.; by C. L. Wagner, between 1 and 3 days for a 0.00042*M*-soln. at 25°; by E. Heymann, many months for a 0.005 soln. at 20°, and 1 to 2 months at 37°; and by G. Fousseureau, for a 0.01*M*-soln., 30 mins. at 100°, 80 mins. at 84°, and above 74 days at ordinary temp. G. Fousseureau, E. Heymann, G. Malfitano, and G. Malfitano and L. Michel found that the process of hydrolysis is reversible when it has been slowly attained. The same final state can be obtained by starting from either end of the system. The hydrolysis  $\text{FeCl}_3 + 3\text{H}_2\text{O} \rightleftharpoons 3\text{HCl} + \text{Fe}(\text{OH})_3$  is displaced from left to right by raising the temp. or diluting the soln.; and when the state of equilibrium has been displaced from left to right by raising the temp., the original state is restored when kept at ordinary temp. G. Fousseureau observed that the state of equilibrium is reversibly displaced in favour of increasing hydrolysis by raising the pressure; and A. Dumansky found that centrifuging the soln. in equilibrium, results in extending the hydrolysis. B. E. Moore observed that light had no effect on the hydrolysis, but G. Fousseureau said that some of the hydrosol of ferric hydroxide may be coagulated, and H. Schild, and P. Roeser added that the coagulation occurs only when some ferrous chloride is present. S. S. Bhatnagar and co-workers found that exposure to X-rays favours the hydrolysis. H. M. Goodwin and F. W. Grover observed that a magnetic field of 1850 gauss had no perceptible influence on the hydrolysis.

The presence of hydrochloric acid hinders the hydrolysis, and, as shown by A. Byk and H. Jaffe, if a soln. of ferric chloride be diluted until it is colourless, and conc. hydrochloric acid be added, the soln. assumes the brown colour characteristic of molecular ferric chloride. G. Malfitano and L. Michel showed that the initial quiescent period of constant conductivity increases with the proportion of added hydrochloric acid, and, other things being equal, the proportion of acid required



to render the soln. stable increases considerably with the temp. and varies slightly with the conc. of the ferric chloride. During the hydrolysis of a ferric chloride soln., a considerably larger quantity of hydrochloric acid can be formed than would have rendered the soln. stable if added at first, the conductivity of hydrolyzed soln. rising to values greater than those of soln. initially treated with acid. Moreover, small additions of acid only retard hydrolysis at the beginning, they afterwards accelerate it. The increase in conductivity on heating, and its decrease subsequently, diminish as the quantity of acid added increases. The conclusion is drawn that the products of hydrolysis are not constant in composition, only those first formed being easily reconverted into  $\text{FeCl}_3$  by the hydrochloric acid present, the action of the acid becoming more and more difficult as the hydrolysis progresses, and, further, that the products of hydrolysis are rendered more resistant by the presence of hydrogen chloride. The amount of hydrochloric acid which, added at the beginning, renders the soln. stable, when added during hydrolysis, not only does not restore the soln. to its original condition, but does not stop the hydrolysis. These phenomena are best explained by the hypothesis that the colloid formed from the products of hydrolysis is composed of complex ions. The precipitation of ferric colloids by anions diminishes as the valency of the latter increases, and it is inferred that the anions act similarly in preventing the formation of the colloid. The activity of nitric, oxalic, hydrochloric, sulphuric, arsenic, or phosphoric acid at conc.  $0.001N$ -,  $0.004N$ -, and  $0.01N$ -, on  $\frac{1}{150}N$ - $\text{FeCl}_3$ , in increasing the conductivity is a function of the time; and their activity in retarding the progress of irreversible hydrolysis, is partly dependent on their degree of ionization, but the influence of the anion is shown by differences in the activity between equally ionized acids, such as hydrochloric and nitric acids, and particularly by the activity of oxalic acid which is much greater than would be anticipated from its ionization coeff. As the concentration of the acid diminishes, the influence of the  $\text{H}^+$ -ions becomes negligible, and that of the polyvalent anions preponderant—probably through the replacement of chlorine in ferric chloride, and the formation of molecules with a smaller tendency to dissociate. The increase with time of the conductivity of the  $\frac{1}{150}N$ - $\text{FeCl}_3$ , containing variable proportions of phosphoric acid is least when the conc. of the acid is  $0.004N$ - $\text{H}_3\text{PO}_4$ ; at lower conc., the hydrolysis and formation of colloid are only slackened, and at higher conc., the formation of colloid is definitely prevented, the conductivity meanwhile increasing with time. This can be explained only by the quantity of free hydrochloric acid displaced by the phosphoric acid. The phenomenon becomes more evident at  $100^\circ$ ; soln. of ferric chloride containing an eq. of phosphoric acid, when heated at this temp., give a white positive colloid containing iron and phosphoric acid, which tends to disappear on cooling the more easily the greater is the conc. of the ferric chloride. The formation of the hydroxide colloid is prevented when the ratio  $\text{Fe} : \text{PO}_4$  is  $1 : 6000$  at  $18^\circ$ ;  $1 : 200$  at  $50^\circ$ ; and  $1 : 16$  at  $100^\circ$ . An increase in the temp. and dilution affects only the irreversible, not the reversible, hydrolysis. It is concluded that the ferric ions become less apt to form complex ions,  $(\text{Fe}[\text{Fe}(\text{OH})_3]_n)$ , as the valency of the accompanying anions increases, and the micro-cells, conceived as complex ions of large dimensions ( $n$  being very great), protect the mols of the hydroxide from the hydrochloric acid. Consequently, if these complex ions cannot be formed, the irreversible hydrolysis is impeded. G. Malfitano and L. Michel conclude that the phenomena of the colloidal state are more pronounced and appear more rapidly in soln. of ferric chloride to which potassium chloride has been added than in soln. of ferric chloride alone. The rate of hydrolysis of the ferric chloride depends on the proportion of potassium chloride present. The size of the micro-cells of ferric hydroxide is increased by the addition of this salt. The number of ferric ions being diminished, there are fewer centres of attraction for the ferric hydroxide molecules, and consequently the individual cells are more voluminous. The chlorides of sodium, ammonium, barium, and magnesium, and also potassium nitrate, behave in a similar manner. Mercuric chloride, on the other hand, being a

non-electrolyte, has no appreciable influence on the course of the hydrolysis. Salts containing polyvalent negative ions, such as potassium sulphate, behave like the polyvalent acids previously studied in hindering hydrolysis. The influence of potassium sulphate on the hydrolysis was examined by G. Malfitano and L. Michel, A. Quartaroli, and C. L. Wagner; of sodium, barium, and aluminium chlorides, by T. Katsurai; and the action of neutral salts, by G. Malfitano, and G. Malfitano and L. Michel. C. L. Wagner, A. Tian, and N. R. Dhar and D. N. Chakravarti found that gelatine retards the hydrolysis; so does glycerol; and, according to R. Phillips, sugar. The action of silica-gel was studied by A. Tian, and N. R. Dhar and D. N. Chakravarti.

When the dil. aq. soln. of ferric chloride is aged, or heated, a hydrogel of ferric hydroxide (*q.v.*) is formed. H. M. Goodwin and F. W. Grover found that the effect of lowering the temp. is to diminish the rate of formation of the colloidal hydrated ferric oxide, and of the separation of the hydrogel. Soln. of 0.02*N*-, and 0.002*N*-FeCl<sub>3</sub> remained quite clear when kept on ice for 2 weeks; but a 0.0075*N*-soln. became very turbid in less than 4 days at 25°, slightly turbid in the same time at 15°; and it remained clear at 0°. The subject was investigated by A. Béchamp, H. Debray, H. W. Fischer, H. M. Goodwin and co-workers, F. W. C. Krecke, G. Malfitano, T. Katsurai, P. Nicolardot, S. U. Pickering, C. R. C. Tichborne, H. B. Weiser, etc. It was formerly thought that the formation of the precipitate was a measure of the progress of the hydrolysis; but E. Heymann and others have emphasized the fact that the coagulation of the hydrosol is not related with the hydrolysis in any simple manner. The conditions necessary to ensure the reproduction of phenomena have not yet been all recognized.

According to H. M. Goodwin, the phenomena which attend the primary hydrolysis of the soln. of ferric chloride can be explained by assuming that a reaction symbolized:  $\text{FeCl}_3 + \text{H}_2\text{O} = \text{Fe}(\text{OH})^{++} + \text{H} + 3\text{Cl}^-$ , or  $\text{Fe}^{+++} + \text{H}_2\text{O} = \text{Fe}(\text{OH})^{++} + \text{H}^+$ , occurs. The base  $\text{Fe}(\text{OH})^{++}$  may be formed in soln. in accord with  $\text{Fe}(\text{OH})_3 \rightleftharpoons \text{Fe}(\text{OH})^{++} + 2\text{OH}^-$ , and the supposed step-by-step ionization of polybasic acids. The first result of diluting a soln. of ferric chloride, as shown by conductivity measurements, is to inaugurate the reaction:  $\text{FeCl}_3 + \text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})\text{Cl}_2 + \text{HCl}$ . B. E. Moore considered that optical observations supported H. M. Goodwin's views of the formation of  $\text{Fe}(\text{OH})\text{Cl}_2$ , as an intermediate product of the hydrolysis; but C. L. Wagner doubted the hypothesis. W. C. Bray and A. V. Hershey studied the system:  $\text{Fe}^{+++} + \text{Cl}^- = \text{FeCl}^{++}$ . According to H. M. Goodwin, assuming that the  $\text{Fe}(\text{OH})^{++}$ -ions are colourless, the hypothesis is in agreement with the fact that the first effect of the dilution is to reduce the coloration of the soln. The increase of the conductivity is attended by a deepening of the colour of the soln. until the colour is the same as that of the colloidal hydroxide obtained by T. Graham,  $n\text{Fe}(\text{OH})^{++} + 2n\text{H}_2\text{O} = \{\text{Fe}(\text{OH})_3\}_n + 2n\text{H}^+$ . It is here assumed that the colloidal hydroxide is a polymeric form of the normal hydroxide. A. P. Sabanéeff favours the assumption that the colloid has the formula  $\text{FeCl}_3.n\text{Fe}(\text{OH})_3$ , where *n* is very great. The reaction at this stage is almost irreversible.

According to C. L. Wagner, the hydrolysis is very rapid, and the hydrated oxide is liberated as a highly dispersed phase, and the liberating acid is completely adsorbed on the enormous surface of this dispersed phase. As the particles increase in size in the process of time, the surface of the dispersed phase rapidly diminishes, and the adsorbed acid enters the soln., and this is taken to explain the increase in conductivity which occurs when the requisite dilution is reached. The hypothesis is supported by an ultra-microscopic examination of dil. soln. of ferric chloride. According to E. Heymann, when a freshly prepared soln. of ferric chloride is allowed to stand, the whole of the products of hydrolysis pass through an ultra-filter, but the degree of dispersion decreases with increasing age, and the proportion of the iron finally in the colloidal state increases with a rise in temp. and with a decrease in the conc. of the salt. This quantity may correspond

with an actual equilibrium because if a ferric chloride soln. be heated at 80° for 45 mins., whereby the hydrolysis is almost completed, and then aged at 20° or 37°, the amount of colloid ultimately approximates to that corresponding with the final temp. On the other hand, there is less chlorine in the colloid produced at 80° than in those produced at lower temp., and the amount does not change on cooling. The increase in the conductivity of the chloride soln. with age runs parallel with the colloid content except immediately after the soln. has been prepared, when the conductivity increases the more rapidly, as would be expected in view of the initial high degree of dispersion of the products of hydrolysis. The micelles themselves possess a measurable conductivity, but although with increasing age of the soln. they increase in quantity, their relative contribution to the conductivity of the system diminishes. This may be due in part to changes in dispersion, yet chemical changes are also involved, since the amount of chlorine falls at the same time, the composition of the final products of slow hydrolysis corresponding, not with a hydroxide, but with an oxychloride. As suggested by P. Nicolardot, it appears likely that the first product of hydrolysis is an oxychloride of the type  $\text{FeCl}_n\text{Fe}(\text{OH})_3$ , where  $n$  is probably less than 9. The mols. of this compound tend to associate, *i.e.* coagulate, and react with water with the elimination of hydrogen chloride and the formation of secondary oxychlorides which increase in complexity until their mols. attain colloidal dimensions. The original state of equilibrium is consequently disturbed, and more and more ferric chloride is hydrolysed—*vide supra*, the hydrated oxide.

E. Heymann observed that the relation:  $[\text{HCl}]^3 = K[\text{FeCl}_3]$  is only approximate in the case of colloidal ferric hydroxide, and hydrochloric acid, because, for a given concentration, the amount of ferric chloride formed increases with the concentration of the ferric hydroxide. The active mass of the colloidal product of the hydrolysis of ferric chloride is not constant, but increases with the concentration of the colloid. The reaction between colloidal ferric hydroxide and hydrochloric acid takes place, not only on the surface of the particles, but also within the surface. The equilibrium is also influenced by the degree of dispersion of the ferric hydroxide: thus, coarsely dispersed ferric hydroxide is in equilibrium with a smaller concentration of ferric chloride than the highly dispersed colloid. The dispersity varies with age, and by altering this condition micelles of different chemical composition can be produced. The micelles richest in chlorine are obtained by the ageing of ferric chloride solutions and those poorest in chlorine by mixing ferric hydroxide sol with hydrochloric acid.

The hypothesis of C. L. Wagner on the period of acceleration in the conductivity of the soln. was discussed by A. Quartaroli, A. Tian, E. I. Spitalsky and co-workers, and U. Antony and G. Giglio. The hypothesis of H. M. Goodwin, that during the primary hydrolysis  $\text{Fe}(\text{OH})^{++}$ -ions accumulate in the system, involves the further assumption that as the hydrolysis proceeds, the reaction:  $\text{Fe}(\text{OH})^{++} + 2\text{H}_2\text{O} = \text{Fe}(\text{OH})_3 + 2\text{H}^+$  is inaugurated. The initial lag, and the acceleration in the rate of the reaction are attributed to the rate of formation of the colloidal hydroxide being dependent on the presence of a certain amount of the colloid itself, which acts as in the analogous case when the rate of crystallization is a function of the number of nuclei about which crystals can form. This hypothesis is supported by the observation that an addition of less than 2 eq. per cent. of the colloidal hydroxide to 0.0075N- $\text{FeCl}_3$  at 25° accelerates the reaction to a marked degree. The observed initial lag of 20 mins' duration is almost entirely eliminated. The increase in the initial rate of the reaction is approximately proportional to the conc. of the added colloid. B. E. Moore found that the hydrated oxide prepared by dialysis is less active than that prepared by the hydrolysis of ferric chloride. The greater speed of the reaction in dil. soln. is attributed to the presence of a larger proportion of  $\text{Fe}(\text{OH})^{++}$ -ions, and of colloidal ferric oxide. The hypothesis that the secondary period is due to the passage of  $\text{Fe}^{+++}$ -ions, to non-ionized, colloidal hydroxide was discussed by U. Antony and G. Giglio, N. R. Dhar and

D. N. Chakravarti, H. M. Goodwin, J. Traube and W. von Behren, E. Heymann, G. Malfitano, G. Malfitano and M. Sigaud, M. Neidle, and A. Tian.

Other interpretations of the mechanism of the hydrolysis have been given. W. Spring, and W. Jufereff favoured the assumption that the ferric chloride dissociates in soln. the same as it does in the gaseous state, to form ferrous chloride and chlorine,  $\text{Fe}_2\text{Cl}_6 \rightleftharpoons \text{Fe}_2\text{Cl}_4 + \text{Cl}_2$ , or  $\text{Fe}_2\text{Cl}_4 \cdot \text{Cl}_2$ , and that the chlorine then reacts with water to form hydrogen chloride and oxygen; and that the latter combines with ferrous chloride to form the oxychloride,  $\text{Fe}_2\text{OCl}_4$ , until the equilibrium  $2\text{FeCl}_2 + \text{H}_2\text{O} + \text{Cl}_2 \rightleftharpoons \text{Fe}_2\text{OCl}_4 + 2\text{HCl}$ , is attained. This is supposed to explain the augmented conductivity of soln. of concentration greater than 3.6 litres per mol. H. Querengässer measured the electrical conductivity of the vapour of ferric chloride. A. Dumansky and T. A. Granskaya measured the difference of potential established when electrodes of unequal surface are set up in a cell with ferric ions to which aq. ammonia is progressively added.

The **degree of hydrolysis** of aq. soln. of ferric chloride has been measured, but the soln. in all cases have probably not been in a state of equilibrium. F. W. C. Krecke studied the process of hydrolysis by measuring the sp. gr. of the soln.; F. L. Browne and J. H. Mathews, and G. Lemoine, the heat of dilution; and H. M. Goodwin, the lowering of the f.p. of the soln. U. Antony and G. Giglio made colorimetric observations on the percentage degree of hydrolysis,  $\beta$ , with soln. containing  $C$  mols per litre, and found, at  $12^\circ$  after 48 hrs.:

$C$	.	.	0.020466	0.006822	0.002047	0.001023	0.000512	0.000256
$\beta$	.	.	0.6	23.55	45.25	56.12	65.74	79.03

B. E. Moore studied the process by measuring the absorption spectrum, and T. Ewan, the extinction coeff. In the latter case, with soln. aged for many weeks at  $15^\circ$  to  $16^\circ$ :

$C$	.	.	0.005050	0.002525	0.001263	0.000505	0.000101	0.00002525
$\beta$	.	.	36.83	50.10	64.77	82.7	86	100

H. M. Goodwin calculated from the electrical conductivity at  $25^\circ$  the value  $\beta$ , on the assumption that the reaction is  $\text{FeCl}_3 + \text{H}_2\text{O} = \text{Fe}(\text{OH})^{++} + 3\text{Cl}' + \text{H}'$ ; and the value  $\beta_2$  on the assumption that the reaction is  $\text{FeCl}_3 + 3\text{H}_2\text{O} = \text{Fe}(\text{OH})_3 + 3\text{HCl}$ —*vide infra*. The results were also re-calculated by N. Bjerrum. G. Wiedemann based his calculations on his measurements of the molecular magnetism of the soln. Calculations based on measurements of the action of the soln. on iodides were made by N. Sasaki; on the activity of chlorides, by F. L. Browne; on the decomposition of diazoacetic ether, by A. Quartaroli; on the hydrolysis of methyl acetate, by G. Carrara and G. B. Vespignani; on the inversion of cane-sugar, by A. Fodor and A. Rosenberg, and L. Bruner; and on the products of ultra-filtration, by E. Heymann. J. N. Brönsted and K. Volqvartz studied the acid hydrolysis of the salt.

Attempts have been made by F. L. Browne, N. R. Dhar and G. Urbain, H. M. Goodwin, H. C. Jones and co-workers, R. Lorenz, R. Peters, and N. Sasaki to calculate the **degree of ionization**,  $\alpha$ , of the salt in soln. The results are complicated by the ionization of the products of the hydrolysis. On the assumption that the ionization and hydrolysis proceed in accord with the reactions (i)  $\text{FeCl}_3 \rightleftharpoons \text{Fe}^{+++} + 3\text{Cl}'$ ; and (ii)  $\text{FeCl}_3 + \text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})^{++} + \text{H}' + 3\text{Cl}'$ , H. M. Goodwin showed that for equilibrium, the soln. contains  $1-\alpha-\beta$  mol of  $\text{FeCl}_3$ ;  $\alpha$  mol of  $\text{Fe}^{+++}$ ;  $3\alpha$  mols of  $\text{Cl}'$ ;  $\beta$  mol of  $\text{Fe}(\text{OH})^{++}$ ;  $\beta$  mol of  $\text{H}'$ ; and  $3\beta$  mol of  $\text{Cl}'$ . Measurements of the electrical conductivity on the f.p. of the soln. show that with soln. of eq. concentration  $C$ :

$C$	.	.	0.30	0.15	0.075	0.030	0.015	0.0075	0.0030	0.0015
$\alpha$	.	.	73	77	74	50	35	24	10	5
$\beta$	.	.	—3	2	11	37	53	67	84	91
$\beta'$	.	.	—1	1	4	12	18	22	28	31

where  $\beta'$  denotes the percentage degree of hydrolysis on the assumption that the reaction is  $\text{FeCl}_3 + 3\text{H}_2\text{O} = \text{Fe}(\text{OH})_3 + 3\text{H}^+ + 3\text{Cl}^-$ . The values of  $\beta'$  are taken to show that the assumed reaction is absurd since the hydrolysis would remain nearly constant with increasing dilution. The values of  $\beta$  are taken to be in agreement with the assumption that the hydrolysis proceeds in accord with equations (i) and (ii). W. Hittorf gave 0.254 for the **transport number** of the  $\text{Fe}^{+++}$ -ion in 6.02*N*- $\text{FeCl}_3$ , and 0.400 in 0.705*N*- $\text{FeCl}_3$ ; whilst K. Hopfgartner gave 0.384 for 0.137*N*- $\text{FeCl}_3$ , and 0.359 for 0.444*N*- $\text{FeCl}_3$ , and calculated for infinite dilution 0.396. The acidity of the soln. had no perceptible influence on the results.

H. C. Jones and co-workers calculated the **degree of hydration**, that is, the **solvation**, of the salt in aq. soln., and found that if  $n$  denotes the number of mols of  $\text{H}_2\text{O}$  taken up by a mol of  $\text{FeCl}_3$ , in soln. with  $C$  mols of  $\text{FeCl}_3$  per litre, at  $0^\circ$ :

$C$	0.2	0.4	0.6	0.8	1.0	1.2	1.3617
$n$	61.0	50.7	44.8	39.6	35.4	32.1	29.5

From his observations on the transport numbers, K. Hopfgartner calculated that in a feebly acidified soln. of 0.137*N*- $\text{FeCl}_3$ , the  $\text{Cl}^-$ -ions are each loaded with 6 mols. of  $\text{H}_2\text{O}$ , and each  $\text{Fe}^{+++}$ -ion with 64 mols.; the observations of W. Manchot and co-workers on the solubility of acetylene, indicate that each molecule of  $\text{FeCl}_3$  in soln., with 1.3433 to 2.1558 grms.  $\text{FeCl}_3$  per litre, is loaded with 20.2 to 16.8 mols. of  $\text{H}_2\text{O}$ . A. E. Oxley's, and A. Smits and co-workers' observations on the viscosity; P. P. von Weimarn's observations on the cooling of the soln. to liquid air temp.; A. Brann's, and J. H. Walton and A. Brann's observations on the velocity of freezing; and H. G. Byers and C. H. Walter's, on electro-endosmosis, all agree that the salt is hydrated in aq. soln. L. W. Elder studied the electro-metric titration of soln. of ferric chloride by soln. of sodium hydroxide.

The **electrolysis** of soln. of ferric or ferrous chloride has been discussed in connection with the preparation of iron. Observations were made by H. Buff, A. Geuther, W. Hampe, W. Hittorf, S. I. Levy and G. W. Gray, T. P. McCutcheon and E. F. Smith, J. H. Paterson, etc. F. G. Donnan and H. Bassett found that with soln. of ferric chloride in conc. hydrochloric acid, a brownish-yellow liquid accumulated about the anode indicating the existence of complex iron anions. Z. Karaoglanoff studied the influence of diffusion currents on the electrolytic reduction; H. G. Byers and C. H. Walter, the electro-endosmose, that is, the motion of the electrolyte apart from the movements of the ions; A. Schukareff, the magnetic effect which occurs when the electrolysis occurs in a magnetic field of 2000 to 7000 gauss; M. le Blanc, the polarization; C. Baillod, the depolarizing action of ferric chloride in the cell  $\text{Al}_{\text{amalgam}} | \text{N-H}_2\text{SO}_4, \text{NaCl}_{\text{sat. soln.}} | \text{C}$ ; L. Riéty, the potential difference between a soln. in a capillary at 25 atm. press., and the emerging soln.; and A. Finkelstein, the **decomposition voltage**, where with 0.1*N*-, 0.01*N*-, and 0.001*N*- $\text{FeCl}_3$ , the voltages were respectively -0.82, -0.97, and -0.75. E. Baur observed that the difference in the potential of a soln. against platinum when illuminated and when in darkness is really the result of a small temp. effect. N. Kameyama and K. Takahashi studied the electro-reduction of the salt.

The **electromotive force**, etc., of various cells with an electrolyte containing ferric chloride have been described. Thus, W. E. Case studied the cell  $\text{C} | \text{FeCl}_3 | \text{Pt}$ ; H. Buff, the cells  $\text{Zn} | \text{H}_2\text{SO}_4 | \text{FeCl}_3 | \text{C}$ , and  $\text{Zn} | \text{NaCl} | \text{FeCl}_3, \text{HCl} | \text{C}$ ; A. von Eccher,  $\text{Zn} | \text{H}_2\text{SO}_4 | \text{FeCl}_3 | \text{C}$ , and  $\text{Zn} | \text{H}_2\text{SO}_4 | \text{FeCl}_3 | \text{Pt}$ ; T. Moore,  $\text{Zn} | \text{H}_2\text{SO}_4 | \text{FeCl}_3 | \text{Pt}$  or  $\text{C}$ ; E. Duchemin,  $\text{Zn} | \text{FeCl}_3(\text{Br}) | \text{H}_2\text{SO}_4 | \text{C}$ ; E. Petersen,  $\text{Zn} | \text{NaCl} | \text{FeCl}_3 | \text{Cl}$ ; H. N. Warren,  $\text{Zn} | \text{FeCl}_3, \text{Br} | \text{C}$ ; L. Kahlenberg,  $\text{Pt} | 0.3\text{N-FeCl}_3 | \text{N-KCl, Hg}_2\text{Cl}_2 | \text{Hg}$ , and  $\text{Pt} | 0.3\text{N-FeCl}_3 | 0.375\text{N-FeCl}_3$  in amyl alcohol  $| \text{Pt}$ ; N. Sasaki and K. Nakamura,  $\text{Pt} | \text{KI, FeCl}_3, \text{NaCl} | \text{KCl} | \text{N-KCl, Hg}_2\text{Cl}_2 | \text{Hg}$ ; and W. D. Bancroft,  $\text{Pt} | \text{FeCl}_3 | \text{Solution} | \text{Pt}$ , where the "solutions" employed were  $\text{KCl, Cl}$ ;  $\text{KBr, Br}$ ;  $\text{KOH, Cl}$ ;  $\text{KOH, Br}$ ;  $\text{KI, I}$ ;  $\text{KClO}_3, \text{H}_2\text{SO}_4$ ;  $\text{KClO}_4, \text{H}_2\text{SO}_4$ ;  $\text{KIO}_3, \text{H}_2\text{SO}_4$ ;  $\text{NaSO}_3$ ;  $\text{NaHSO}_3$ ;  $\text{KNO}_2, \text{H}_2\text{SO}_4$ ;  $\text{HNO}_3$ ;  $\text{KMnO}_4, \text{H}_2\text{SO}_4$ ;  $\text{MnO}_2, \text{HCl}$ ;  $\text{H}_2\text{Cr}_2\text{O}_7$ ; and  $\text{K}_2\text{Cr}_2\text{O}_7$ .

H. N. Warren observed that if bromine and a conc. soln. of ferric chloride be used in place of the dichromate in the dichromate cell, the e.m.f. is greater. L. Kahlenberg found that with a cell  $\text{Pt} | A | C | \text{Pt}$ , where  $A$  represents a soln. of 1.4508 grms. of  $\text{FeCl}_3$  in 77.6 c.c. of nitrobenzene, and  $C$ , a 0.375*N*- $\text{FeCl}_3$  soln. in ethyl alcohol, the e.m.f. is 0.792 volt at 20°; and with the cell  $\text{Pt} | B | C | \text{Pt}$ , where  $B$  denotes a soln. of 0.1473 grms. of  $\text{FeCl}_3$  in 10 c.c. of *o*-nitrotoluene, the e.m.f. is 0.623 volt. G. Tammann and E. Jenckel observed that in the cell  $\text{Pd}(\text{H}_2) | 0.1\text{N-HCl}, \text{FeCl}_3 | 0.1\text{N-HCl}, \text{Hg}_2\text{Cl}_2 | \text{Hg}$ , at 18°, when the ferric chloride soln. is under a press.,  $p$  kgrms. per sq. cm., the e.m.f.,  $E$  volts, is:

$p$	1	100	500	1000	1500	2000	2500	3000
$E$	0.4910	0.4901	0.4867	0.4831	0.4794	0.4759	472.4	0.4690
$dE/p \times 10^3$		-9.0	-8.6	-7.9	-7.7	-7.6	-7.4	-7.3

G. E. Gibson and W. A. Noyes found the **spark potential** in the vapour of ferric chloride is greater than it is in air. J. A. Fleming and J. Dewar found the **dielectric constant** (vacuum unity) for a sat. soln. of frozen ferric chloride at -198.8°, -162.7°, -144.9°, and -133.8° to be respectively 3.34, 3.56, 3.91, and 4.23. O. Milicka and A. Slama, and R. Fürth measured the dielectric constant of soln. of the salt.

According to M. Faraday, anhydrous ferric chloride is paramagnetic and, added C. Matteucci, neither the hexahydrate nor the anhydrous salt shows remanent magnetism. G. Wiedemann found that the **magnetism** of anhydrous ferric chloride is rather greater than is that of ferrous chloride with an equivalent proportion of iron, and is but little different from the value for the salt in aq. soln. A. Heydweiller observed that the equivalent magnetism of ferric chloride is scarcely any greater when in soln. than when it is in the form of the hexahydrate; the ratio is 1.006:1. E. Feytis gave for the molecular **magnetic susceptibility**,  $14,652 \times 10^{-6}$  at 13°, and for the magnetic susceptibility  $\chi = 102.5 \times 10^{-6}$  mass unit; G. Meslin gave  $\chi = 102.5 \times 10^{-6}$ ; and T. Ishiwara,  $\chi = 93.4 \times 10^{-6}$ . T. Ishiwara's values for temp. below 44.6°, and K. Honda and T. Ishiwara's values for higher temp., in fields of about 2000 gauss, are:

	-170.4°	-147.0°	-62.5°	-3.7°	20°	69.7°	134.8°	194.9°	261.3°
$\chi \times 10^6$	252.0	195.5	121.0	94.5	86.2	73.8	60.9	50.4	35.6

The decrease from -190° to 200° is approximately in accord with  $\chi T = \text{constant}$ , but at higher temp. there are deviations which are attributed to the disturbing effects of sublimation, or the formation of an oxychloride. H. R. Woltjer and E. C. Wiersma found that the sp. susceptibility of the anhydrous salt depends on the absolute temp.,  $T$ , in the formula  $\chi(T - \theta) = \text{constant}$ , down to -210°. The inversion temp., or Curie point, is  $\theta = -252.6^\circ$ . Above -180°, the susceptibility is independent of the intensity of the magnetic field. Anomalies occur at the temp. of liquid hydrogen, for the susceptibility then becomes independent of the intensity of the magnetic field, and the relation with temp. is the opposite to what it is at higher temp. H. Mosler found that the temp. coeff. of the susceptibility between 0° and 40° is 0.00326, a value a little greater than that of the hydrated salt. G. Berndt gave for the magnetic susceptibility  $\chi = 47.5 \times 10^{-6}$  mass unit, and for the hexahydrate,  $76.1 \times 10^{-6}$ . L. A. Welo measured the temp. coeff. of the susceptibility, the magnetic susceptibility, and the Curie point of the liquid and solid hexahydrate. The results are plotted in Fig. 580. In the formula  $\chi(T - \theta) = \text{constant}$ , Curie's constant for the solid is 4.82, and for the liquid,

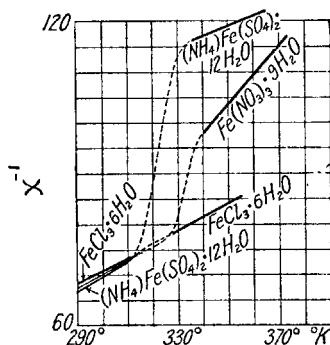


Fig. 580.—The Magnetic Susceptibility of Hydrated Ferric Salts —Molten and Solid.

3.79; whilst the Curie point, or the inversion temp.,  $\theta$ , is  $-36^\circ$  for the solid, and  $34^\circ$  for the liquid. G. Berndt observed that the hysteresis of the hexahydrate in a field of 200 to 400 gauss cannot be detected.

M. Faraday observed that conc. aq. soln. of ferric chloride are paramagnetic. L. Külpe showed that a glass tube filled with the aq. soln. which has been magnetized in a definite direction for a long time requires for magnetization in the opposite direction less magnetism than before. This, said S. Henrichsen, does not mean that the soln. has a remanent magnetism, because the phenomenon is exhibited by evacuated tubes. C. Matteucci could detect no remanent magnetism; and L. Lombardi, no hysteresis, although P. Drapier observed a slight effect. J. Plücker found that strongly paramagnetic soln. on the poles of a strong magnet exhibit changes on the surface of the liquid. The subject was studied by P. Drapier, H. R. Woltjer and E. C. Wiersma, C. Marangoni, and A. Quartaroli. C. Stasescu observed changes in the conc. of a conc. soln. of ferric chloride near a strongly magnetic pole; and the phenomenon was studied by L. Abonnene, G. Falckenberg, P. Drapier, F. Ehrenhaft and E. Wasser, J. Jamin, J. Plücker, A. Quartaroli, W. Rathert, A. Righi, and W. Voigt and C. Stasescu. P. W. Selwood observed a slow decrease in the paramagnetism of the soln. on exposure to light. G. Jäger and S. Meyer found that the magnetic susceptibility of an aq. soln. of ferric chloride is  $\chi = 73 \times 10^{-6}$  mass unit at  $18^\circ$ ; J. S. E. Townsend gave  $92 \times 10^{-6}$  at  $10^\circ$ ; G. Quincke,  $91 \times 10^{-6}$  at  $19^\circ$ ; O. Liebknecht and A. P. Wills,  $83 \times 10^{-6}$  at  $18^\circ$ ; J. Königsberger,  $88 \times 10^{-6}$  at  $18^\circ$ , and  $92 \times 10^{-6}$  at  $21^\circ$ ; and G. Falckenberg,  $87 \times 10^{-6}$  at  $15^\circ$ . Observations were also made by A. Arndtsen, H. Becquerel, H. E. J. G. du Bois, J. Borgmann, H. W. Eaton, A. von Ettinghausen, G. G. Gerosa and G. Finzi, S. Henrichsen, A. Lallemand, L. Lombardi, P. Pascal, G. Piaggese, J. Plücker, S. Prakash, A. Quartaroli, J. Schuhmeister, P. Siloff, T. Wähner, and G. Wiedemann. According to B. Cabrera and E. Moles, the sp. susceptibility  $\chi$  mass units, and the molecular susceptibility,  $\chi$  mol mass units, at temp. between  $18.37^\circ$  and  $19.95^\circ$ , are:

FeCl <sub>3</sub> .	0.2105	0.4162	0.8247	0.2351 per cent.
$\chi \times 10^6$ .	-0.5545	-0.3865	-0.0541	0.2924
$\chi_{\text{mol.}} \times 10^6$ .	12,700	13,000	13,130	13,260
FeCl <sub>3</sub> .	2.3864	4.8260	9.0710	14.8630 per cent.
$\chi \times 10^6$ .	1.3022	3.4670	7.2547	12.440
$\chi_{\text{mol.}} \times 10^6$ .	13,700	14,050	14,210	14,310

For soln. of ferric chloride with [HCl] mol of HCl per mol of FeCl<sub>3</sub>, at  $18.62^\circ$  to  $21.12^\circ$ :

FeCl <sub>3</sub> .	0.8431	0.8610	0.8221	0.8007 per cent.
[HCl] .	1.54	0.480	1.224	6.923
$\chi \times 10^6$ .	-0.01288	0.04832	0.02781	0.012340
$\chi_{\text{mol.}} \times 10^6$ .	13,540	14,410	14,740	14,780
FeCl <sub>3</sub> .	3.3060	0.3046	0.32290	0.3119 per cent.
[HCl] .	0.0294	0.1521	0.3116	1.6120
$\chi \times 10^6$ .	2.1448	2.2618	2.2393	2.2227
$\chi_{\text{mol.}} \times 10^6$ .	13,990	14,580	14,790	15,210

The vol. susceptibility was also measured by A. Quartaroli; and the mol. susceptibility by A. Heydweiller, G. Falckenberg, P. Pascal, and A. Quartaroli. B. Cabrera and E. Moles noticed that the addition of hydrochloric acid drives back the hydrolysis, and raises the susceptibility. A. Quartaroli found the susceptibility is independent of the age of the soln., although the electrical conductivity, colour, and turbidity change. G. Wiedemann observed that the mol. magnetism decreases slowly as conc. soln. are diluted in consequence of hydrolysis; and if hydrochloric acid be added, the mol. magnetism is raised. A. Quartaroli found for soln. of *C* grms. of FeCl<sub>3</sub> in 100 c.c. of methyl alcohol, between  $17^\circ$  and  $22^\circ$ , for field-strengths of *H* gauss, the mol. susceptibility  $\chi_{\text{mol.}}$  mass units:

FeCl <sub>3</sub> (C) .	2.135	4.271	4.271	16.85	25.39	25.39	50.78	101.56
H .	32,000	32,000	32,000	14,100	14,100	9,700	9,700	9,700
χmol. × 10 <sup>6</sup> .	14,789	16,066	16,098	17,883	18,846	19,058	19,064	18,479

Observations were also made by G. Quincke, R. Blondlot, and T. Wöhner on soln. in methyl alcohol; by M. Faraday, G. Wiedemann, A. E. Oxley, and J. S. E. Townsend, in ethyl alcohol. A. Quartaroli found for soln. with C grms. of FeCl<sub>3</sub> in 100 c.c. of ethyl alcohol, between 17° and 22°:

FeCl <sub>3</sub> (C) .	1.843	3.986	7.972	15.945	15.945	31.89	63.78	127.56
H .	32,000	32,000	18,400	18,400	9,000	9,000	9,000	9,000
χmol. × 10 <sup>6</sup> .	14,748	16,175	16,848	18,643	18,853	18,708	16,836	16,544

Similarly with soln. in isobutyl alcohol:

FeCl <sub>3</sub> . .	4.411	8.223	8.223	16.647	16.647	31.295	70.59	
H .	25,000	25,000	17,000	17,000	11,400	9,600	9,600	
χmol. × 10 <sup>6</sup> .	17,064	17,038	17,203	17,200	17,392	17,592	16,992	

with isoamyl alcohol:

FeCl <sub>3</sub> . .	4.12	8.24	16.48	32.96	32.96	65.92	131.84	
H .	25,000	25,000	11,700	11,700	8,600	8,600	8,600	
χmol. × 10 <sup>6</sup> .	16,092	16,298	17,855	18,364	18,687	17,252	17,395	

with allyl alcohol:

FeCl <sub>3</sub> . .	4.062	8.123	16.25	16.25	32.50	65.00	130.00	
H .	23,300	23,300	23,000	6,000	6,000	6,000	6,000	
χmol. × 10 <sup>6</sup> .	15,940	16,110	17,541	18,045	17,608	17,525	17,333	

with ethyl ether:

FeCl <sub>3</sub> . .	2.262	4.255	9.15	18.30	18.30	36.60	73.20	
H .	25,000	25,000	25,000	15,500	8,200	8,200	8,200	
χmol. × 10 <sup>6</sup> .	17,878	19,183	18,697	18,222	18,679	17,343	16,282	

Observations were also made by G. Wiedemann, and P. Drapier. A. Quartaroli found for soln. in acetone:

FeCl <sub>3</sub> . .	1.786	3.573	3.573	14.293	28.587	28.587	51.175	114.35
H .	32,000	32,000	25,000	11,800	11,800	7,200	7,200	7,200
χmol. × 10 <sup>6</sup> .	14,795	15,606	15,707	18,009	16,878	17,574	17,073	16,271

with soln. in formic acid:

FeCl <sub>3</sub> . .	6.67	13.34	26.68	26.68	53.37	53.37	106.74	
H .	25,000	25,000	18,400	10,000	10,000	7,500	7,500	
χmol. × 10 <sup>6</sup> .	1,528	15,736	16,576	16,696	16,599	17,408	17,598	

with soln. in acetic acid:

FeCl <sub>3</sub> . .	3.035	3.035	6.07	12.14	24.28	48.56	48.56	97.12
H .	32,000	25,000	25,000	25,000	12,000	12,000	9,200	9,200
χmol. × 10 <sup>6</sup> .	17,397	17,387	17,485	16,905	18,204	17,364	17,509	17,017

with a soln. of 6.870 grms. of paramagnetic ferric chloride in a litre of diamagnetic methyl acetate, A. Quartaroli observed that the soln. is magnetically inactive; and with ethyl acetate:

FeCl <sub>3</sub> . .	2.327	4.658	4.658	9.716	38.867	38.867	77.735	155.47
H .	32,000	32,000	25,000	25,000	10,000	6,000	6,000	6,000
χmol. × 10 <sup>6</sup> .	14,700	15,733	15,764	16,250	18,357	18,395	17,740	16,695

The magnetic rotation of soln. of ferric salts was studied by H. E. J. G. du Bois, H. Becquerel, M. E. Verdet, G. Quincke, A. Cotton, C. E. Richards and R. W. Roberts, and C. V. Raman and S. W. Chinchalkar. G. Wiedemann found that the *temperature coefficient* of the magnetization is smaller with soln. of ferric chloride which are hydrolyzed, than is the case with acidified soln. which are not hydrolyzed. The temp. coeff. of a 30 per cent. soln., between 10.45° and 60.8°, was found by P. Plessner to be 0.003542; G. Jäger and S. Meyer observed that the coeff. ranges between 0.0022 and 0.0029 for 6 to 42 per cent. soln. between 0° and 90°; G. Piaggese gave 0.00277, 0.00283, and 0.00281 respectively for 12.86, 21.14,



and 44.0 per cent. soln. between 24° and 85°. Observations were also made by A. E. Oxley, G. Quincke, J. S. E. Townsend, and R. H. Weber. H. Mosler's results are summarized in Fig. 581. The sp. magnetic susceptibility of the paramagnetic soln. was found by A. Quartaroli to increase with increasing concentration.

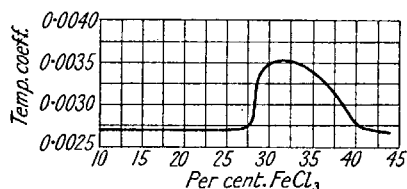


Fig. 581.—Temperature Coefficient of the Magnetic Susceptibility of Solutions of Ferric Chloride.

netically inactive with 6.875 grms. of  $\text{FeCl}_3$  per litre of ethyl acetate; and with pyridine as solvent, with 14,160 grms. of  $\text{FeCl}_3$  per litre. A. Heydweiller observed that the magnetic susceptibility is independent of the *field-strength* up to  $H=40,000$  gauss; and this conclusion is in the main in agreement with the observations of A. Arndtsen, H. E. J. G. du Bois, H. W. Eaton, A. von Ettinghausen, H. Fahlenbrach, G. G. Gerosa and G. Finzi, S. Henrichsen, G. Jäger and S. Meyer, J. Königsberger, L. Lombardi, P. Philipp, P. Siloff, J. S. E. Townsend, T. Wähner, R. H. Weber, and O. Wylach. D. M. Bos and P. K. Raha noted that the paramagnetism decreased in light of a suitable wave-length.

K. Honda and T. Ishiwara calculated the saturation value for the magnetization of a mol of  $\text{FeCl}_3$  to be 32,070, and hence gave  $5.23 \times 10^{23}$  for the **magnetic moment** of the molecule. E. Feytis gave 28.83 for the **magneton number**, and values were also given by B. Cabrera and E. Moles, D. M. Bose, P. Weiss, P. Philipp, and A. Quartaroli. A. Huber discussed the theory of the paramagnetic molecule.

**The chemical properties of ferric chloride.**—According to F. Wöhler, when ferric chloride is heated in dry **hydrogen**, it is first reduced to ferrous chloride, and then to iron (*q.v.*). A. B. Bagdasarian also showed that the reduction proceeds  $\text{FeCl}_3 \rightarrow \text{FeCl}_2 \rightarrow \text{Fe}$ —*vide supra*, ferrous chloride. F. Schmitz said that the metal is pulverulent if obtained at 300° to 400°, but E. Péligot, and W. Spring obtained crystals at a higher temp. A. B. Bagdasarian added that some reduction of the ferric chloride is perceptible at 100°. C. Brunner observed that if hydrogen be passed for 48 hrs. through a dil. aq. soln. of ferric chloride, in darkness, some ferrous chloride is formed; but J. A. Wanklyn and W. J. Cooper, and S. Cooke could not detect any reduction with a conc. soln. kept 48 hrs. in an atm. of hydrogen. F. C. Phillips observed no reduction at room temp., and only a very slight reduction when the soln. was kept at 100° for several hours. W. Ipatéeff and A. I. Kisseleff, and J. H. Weibel obtained a white, easily oxidizable precipitate, by the action of hydrogen at a high press. on a soln. of ferric chloride at 350°. According to F. O. Schmitt and co-workers, soln. of ferric salts are not affected by hydrogen simultaneously exposed to ultrasonic waves. Nascent hydrogen in acid soln.—zinc, iron, aluminium, magnesium, etc.—reduces soln. of ferric chloride to ferrous chloride; the reduction also occurs in neutral soln., but in that case some hydrated ferric oxide is formed. A. C. Cumming and H. Smith showed that an excess of acid retards the reaction. According to D. J. Carnegie, the reduction does not depend on nascent hydrogen because it occurs with ease in absolute alcohol, and it is entirely independent of occluded hydrogen in the zinc. The argument is not conclusive. A. C. Chapman reported that hydrogen occluded in palladium rapidly reduces a soln. of ferric to ferrous chloride; the palladium is not attacked, whilst palladium free from hydrogen is readily attacked by a soln. of ferric chloride. This reduction was discussed by D. J. Carnegie, W. Fresenius, T. Graham, A. Hoenig, H. Gall and W. Manchot, and L. Kritschewsky. D. J. Carnegie observed

that hydrogen occluded in platinum is inactive, and B. Neumann added that hydrogen does not reduce the soln. in the presence of platinum, although S. Cooke observed that the reduction proceeds rapidly and regularly, and H. Gall and W. Manchot found that a hydrochloric acid soln. of ferric chloride in the presence of platinum sponge is quantitatively reduced at room temp.; and A. Pickles, that the soln. is rapidly reduced by hydrogen in the presence of fine copper gauze. W. Biltz and F. Meyer gave  $\text{FeCl}_3.\text{Aq.} + \frac{1}{2}\text{H}_2 = \text{FeCl}_2.\text{Aq.} + \text{HCl.Aq.} + 16.0 \text{ Cals.}$  The reaction was also studied by H. Wolfram, and K. Jellinek and co-workers. W. Biltz and W. Holverscheid gave for the thermal value of the reaction:  $\text{FeCl}_3.\text{Aq.} + \frac{1}{2}\text{H}_2 = \text{FeCl}_2.\text{Aq.} + \text{HCl.Aq.} + 10.3 \text{ Cals.}$  S. Reich and H. O. Serpek said that when **calcium hydride** is added to an ethereal soln. of ferric chloride, hydrogen is evolved and a brown precipitate,  $\text{Ca}_3\text{FeCl}_5(\text{C}_4\text{H}_{10}\text{O})_3$ , is formed.

J. L. Gay Lussac, and A. S. Miller observed that the crystals of anhydrous ferric chloride are very deliquescent when exposed to **air**, forming, according to M. Kinast, and B. Sandrock, pale orange-yellow crystals of the hemipentahydrate. P. Nicolardot added that when the crystals of ferric chloride are exposed to air for a long time at ordinary temp., some hydrochloric acid is given off, and a dirty yellow hydrolysis product remains. C. F. Mohr observed that the hexahydrate is hygroscopic, and J. Fritzsche observed that when exposed to dry air, the salt becomes darker in colour, with an apparent deliquescence, which was found by J. J. Berzelius, and H. Lescœur to be attended by a loss and not a gain of water. H. W. B. Roozeboom said that the hexahydrate can be kept a long time in air without change, but it is hygroscopic, and deliquesces in air when the vap. press. of water exceeds 6 mm. H. W. Hake made some observations on the subject. H. W. B. Roozeboom observed that the hemiheptahydrate is midway between the hexahydrate and the hemipentahydrate in its tendency to deliquesce in air; the hemipentahydrate is stable over conc. sulphuric acid at room temp. J. Fritzsche said that the hemipentahydrate is very deliquescent, and, added F. A. Flücker, it is much more deliquescent than the hexahydrate.

J. L. Gay Lussac observed that when ferric chloride is heated in **oxygen**, chlorine and ferric oxide are formed; and K. Hachmeister added that a similar reaction occurs when the salt is heated in air. H. Schulze found that in oxygen, the reaction begins at dull redness, and that a large proportion of the ferric chloride sublimes unchanged; hence, added G. F. Hüttig and H. Garside, the reaction in dry oxygen is not quantitative. E. W. Wescott added that the vapour of ferric chloride at  $700^\circ$  to  $800^\circ$  is rapidly and completely transformed by air or oxygen into chlorine and ferric oxide. E. W. Wescott obtained ferric oxide and chlorine by burning a spray of ferric chloride in air or oxygen at  $800^\circ$ . The blueing of tincture of guaiacum or of potassium iodide and starch by active oxygen is catalyzed by ferric chloride, and M. J. Gramenitzky found that if the soln. of ferric chloride be boiled and then cooled, the blueing reaction is inhibited, and regenerated if the soln. be left to stand for some time. The effect is attributed to the lowering of the dissociation by heat. The blueing reaction was studied by A. Simon and K. Kötschau.

The solubility of ferric chloride in **water**; the hydrolysis of the salt in aq. soln.; and the alleged volatilization of iron chloride when the aq. soln. is evaporated have been previously discussed. The hydrolysis of the salt accounts for the evolution of more or less hydrochloric acid when the aq. soln. is evaporated. J. Personne said that a neutral soln. of ferric chloride of sp. gr. 1.26 loses some chlorine when it is boiled, and this the more as the soln. becomes more concentrated. R. Stumper showed that the presence of ferric chloride has no appreciable effect on the rate of distillation of water. C. St. Pierre observed that when a dil. soln. acidified with hydrochloric acid is boiled, ferric chloride is not reduced to ferrous chloride, but J. C. Hostetter and H. S. Roberts observed that some reduction occurs when a 10 per cent. soln. is boiled for a short time. M. Schneider could detect no reduction when a conc. and strongly acidified soln. is exposed for a month in

darkness at 20°, but at 100°, some salt was reduced in the course of 12 hrs. J. M. Eder could detect no reduction when the solid salt or the aq. soln. is exposed to light, although H. Hérissé said that some reduction occurs in a soln. exposed to daylight for a long time. F. Kohn also said that the soln. undergoes a slow, very incomplete reduction when it is exposed to light; and M. Schneider added that at 20°, the rate of reduction is augmented by increasing the period of illumination, and by increasing the conc. of the soln. The reduction is not due to the presence of dust, but rather to the photochemical reaction  $2\text{Fe}^{+++} + 2\text{Cl}^- \rightleftharpoons 2\text{Fe}^{++} + \text{Cl}_2$ . R. Audubert, and K. Niederstadt also observed that a reduction occurs in ultra-violet light—*vide supra*. J. L. Gay Lussac observed that when ferric chloride is heated in steam, ferric oxide (hæmatite) and hydrogen chloride are formed. The reaction was studied by A. Daubrée, and E. Puxeddu. P. Nicolardot observed a similar reaction when the hydrated salt is heated.

F. K. Cameron and W. O. Robinson agitated for 3 months an excess of freshly precipitated hydrated ferric oxide with a soln. of ferric chloride, at 25°, and found the solid phases to be those indicated in Table XCII. The composition of the

TABLE XCII.—EQUILIBRIUM OF SOLUTIONS IN THE SYSTEM:  $\text{Fe}_2\text{O}_3\text{--HCl--H}_2\text{O}$  at 25°.

Grms. per 100 grms. sat. soln.		Solid phase	Sp. gr.	Grms. per 100 grms. sat. soln.		Solid phase
$\text{Fe}_2\text{O}_3$	HCl			$\text{Fe}_2\text{O}_3$	HCl	
34.61	59.88	$\text{FeCl}_3 \cdot \text{HCl} \cdot 2\text{H}_2\text{O}$	1.485	21.84	29.33	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O} +$
32.78	54.71	$\text{FeCl}_3 \cdot \text{HCl} \cdot 2\text{H}_2\text{O} +$	1.349	16.82	22.55	$\text{Fe}_2\text{O}_3 \cdot n\text{HCl} \cdot m\text{H}_2\text{O}$
31.95	58.20	$\text{FeCl}_3 + \text{FeCl}_3 \cdot 2\text{H}_2\text{O}$	1.284	14.62	19.53	"
34.42	54.12	$\text{FeCl}_3 \cdot 2\text{H}_2\text{O}$	1.242	10.56	13.76	"
34.21	55.47	$\text{FeCl}_3 \cdot 2\text{H}_2\text{O} +$	1.195	8.60	11.24	"
34.44	51.11	$\text{FeCl}_3 \cdot 3\frac{1}{2}\text{H}_2\text{O} + \text{FeCl}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$	1.158	8.60	11.24	"
33.04	46.72	$\text{FeCl}_3 \cdot 3\frac{1}{2}\text{H}_2\text{O} + \text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	1.070	4.04	5.36	"
24.42	33.42	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	1.047	2.85	3.66	"

solids in equilibrium with soln. with hydrochloric acid ranging from 3.66 to 30.20 per cent., and ferric oxide from 2.85 to 21.84 per cent., were of varying composition and gave no indication of the formation of a definite **ferric oxychloride** at 25°. The stable solid phase is one of a series of solid soln. containing ferric oxide, hydrochloric acid, and water. The solubility of freshly precipitated hydrated ferric oxide in soln. of ferric chloride led R. Phillips, J. M. Ordway, and others to assume that a soluble ferric oxychloride is formed. M. Pettenkofer thought that  $\text{Fe}_2\text{Cl}_6 \cdot 5\text{Fe}_2\text{O}_3$  is formed; J. Jeannel,  $\text{Fe}_2\text{Cl}_6 \cdot 9\text{Fe}_2\text{O}_3$ ; and A. Béchamp,  $\text{Fe}_2\text{Cl}_6 \cdot 12\text{Fe}_2\text{O}_3$ . G. C. Wittstein exposed a soln. of ferrous chloride in air and obtained a precipitate approximating  $\text{Fe}_2\text{Cl}_6 \cdot 6\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$  when dried at 50°; and A. Béchamp evaporated at 100° a soln. of ferrous chloride, and gradually added nitric acid and obtained a yellow precipitate, a similar precipitate approximated, when dried at 100°,  $2\text{Fe}_2\text{Cl}_6 \cdot 25\text{Fe}_2\text{O}_3 \cdot 41\text{H}_2\text{O}$ . This was obtained by boiling for a long time a soln. of ferric chloride in ten times its weight of water. When A. Béchamp's product was treated with water,  $\text{Fe}_2\text{Cl}_6 \cdot 17\text{Fe}_2\text{O}_3$  was formed; and with aq. ammonia,  $\text{Fe}_2\text{Cl}_6 \cdot 72\text{Fe}_2\text{O}_3$ . These products are obviously stages in the hydrolysis of ferric chloride, and there is nothing to show that an indefinitely large number of analogous products would not be obtained by arresting the hydrolysis at different stages of its progress. The subject was also discussed by D. Tommasi, J. Böhm, P. Nicolardot, F. W. C. Krecke, and H. W. Fischer, and also in connection with the hydrosols of ferric oxide.

G. Rousseau heated a mixture of ferric chloride with 10 to 20 per cent. of water in bombs along with lime to remove the hydrogen chloride, and observed that at 150° to 220°, the product of the reaction is  $2\text{Fe}_2\text{O}_3 \cdot \text{Fe}_2\text{Cl}_6 \cdot 3\text{H}_2\text{O}$ , or the *hemihydrate*

of ferric oxychloride,  $\text{FeOHCl} \cdot \frac{1}{2}\text{H}_2\text{O}$ , which appears in doubly refracting, reddish-brown crystals, soluble in dil. acids, and passing into goethite when boiled for 100 to 150 hrs. with water. If the water acts on the ferric chloride at  $220^\circ$  to  $280^\circ$ , the anhydrous chloride,  $\text{FeOCl}$ , is formed; and at  $300^\circ$  to  $340^\circ$ , the complex  $3\text{Fe}_2\text{O}_3 \cdot \text{Fe}_2\text{Cl}_6$ , was said to be produced. The higher the temp. of the reaction, the smaller is the yield of the oxychloride. The reaction at a high temp. may thus involve (i)  $\text{Fe}_2\text{Cl}_6 + 3\text{H}_2\text{O} = \text{Fe}_2\text{O}_3 + 6\text{HCl}$ ; (ii)  $\text{Fe}_2\text{Cl}_6 + 2\text{H}_2\text{O} = 2\text{FeOCl} + 4\text{HCl}$ ; (iii)  $(n+1)\text{Fe}_2\text{Cl}_6 + 3n\text{H}_2\text{O} = n\text{Fe}_2\text{O}_3 \cdot \text{Fe}_2\text{Cl}_6 + 6n\text{HCl}$ ; and (iv)  $\text{Fe}_2\text{Cl}_6 + 6\text{H}_2\text{O} = 2\text{Fe}(\text{OH})_3 + 6\text{HCl}$ ; as well as (v)  $\text{Fe}_2\text{Cl}_6 = 2\text{FeCl}_2 + \text{Cl}_2$ ; and (vi)  $\text{Fe}_2\text{Cl}_6 = 2\text{FeCl}_3$ . The action of heat on ferric chloride alone has been previously discussed. E. Stirnemann studied the action of steam on ferric chloride at high temp., and verified G. Rousseau's observations on the formation of the oxychloride by heating in a steel bomb, 35 to 45 grms. of ferric chloride with 1 to 1.5 grms. of water; after being heated for 1 to 2 hrs., the bomb was cooled in running water. The rhombic plates vary from pale to dark brown, according to their thickness, and those prepared at  $450^\circ$  to  $480^\circ$  have a deep violet lustre. The sp. gr. is 3.1. The crystals become deep violet at  $450^\circ$  to  $480^\circ$ . E. Wedekind and W. Albrecht gave  $\chi = 35 \times 10^{-6}$  for the magnetic susceptibility. The dried salt can be kept in air for a long time, but in the moist state, there is hydrolysis:  $6\text{FeOCl} + 6\text{H}_2\text{O} = 4\text{Fe}(\text{OH})_3 + \text{Fe}_2\text{Cl}_6$ ; and the moist salt in a few days is completely limonitized. At about  $200^\circ$ , in air, a mixture of ferric oxide and hydroxide is formed. When the dry salt is heated in a sealed tube at  $350^\circ$ , the vapour of ferric chloride appears; and similarly at  $450^\circ$ , when the greyish-black residue consists of hexagonal plates of hæmatite, so that the reaction is:  $6\text{FeOCl} = 2\text{Fe}_2\text{O}_3 + \text{Fe}_2\text{Cl}_6$ . N. Costachescu and G. Spacu studied the complex with pyridine,  $\text{FeOCl}_2 \cdot \text{C}_5\text{H}_5\text{N}$ ; and K. A. Hofmann and G. Bugge, the complexes with ethyl carbylamine,  $\text{Fe}_2\text{OCl}_4 \cdot 4\text{C}_2\text{H}_5\text{N}$ , and  $\text{Fe}_2\text{OCl}_4 \cdot 5\text{C}_3\text{H}_5\text{N}$ .

E. Stirnemann studied the equilibrium conditions for the ternary system:  $\text{Fe}_2\text{Cl}_6$ - $\text{FeOCl}$ - $\text{Fe}_2\text{O}_3$ , and the results for the press. and temp. variations are summarized in Fig. 582. A, B, and C represent quadruple points: A, at about

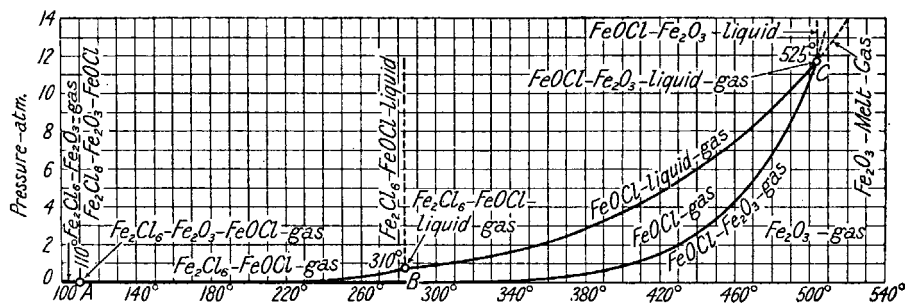


FIG. 582.—Equilibrium Diagrams of the System:  $\text{Fe}_2\text{Cl}_6$ - $\text{H}_2\text{O}$ -Phases.

$110^\circ$ , and  $5 \times 10^{-8}$  atm., refers to  $\text{Fe}_2\text{Cl}_{6\text{solid}}$ ,  $\text{FeOCl}$ ,  $\text{Fe}_2\text{O}_3$ , and gas; B, at  $305^\circ$  and 0.81 atm., refers to  $\text{Fe}_2\text{Cl}_{6\text{solid}}$ ,  $\text{FeOCl}_{\text{solid}}$ , melt, and gas; whilst C, at  $525^\circ$  and 11.7 atm., refers to  $\text{FeOCl}_{\text{solid}}$ ,  $\text{Fe}_2\text{O}_3$ , solid, melt, and gas. Rising from these three points are the almost vertical curves representing the effect of press.; for A,  $dt/dp = 0.05$  atm. (nearly). There is the curve of the vap. press. of ferric chloride over the oxychloride; the boiling curve of ferric chloride in the presence of the oxychloride, and the sublimation curve of ferric chloride in the presence of the oxychloride. Within the area ABC the system is bivariant, with the solid phase  $\text{FeOCl}$ , and to the right of the curve AC, the system is also bivariant with the solid phase  $\text{Fe}_2\text{O}_3$ . The curve AB represents univariant systems, with the solid phases  $\text{Fe}_2\text{Cl}_{6\text{solid}}$  and  $\text{FeOCl}$ ; curve BC likewise, but with molten ferric chloride

and the solid oxychloride, whilst curve *AC* likewise, but with the solids  $\text{Fe}_2\text{O}_3$  and  $\text{FeOCl}$ .

There are three conditions of equilibrium:  $\text{Fe}_2\text{Cl}_6 + 3\text{H}_2\text{O} = \text{Fe}_2\text{O}_3 + 6\text{HCl}$  for which  $K_1[\text{HCl}]^6 = [\text{H}_2\text{O}]^3[\text{Fe}_2\text{Cl}_6]$ , where the bracketed symbols refer to partial press., similarly for  $\text{Fe}_2\text{Cl}_6 + 2\text{H}_2\text{O} = 2\text{FeOCl} + 4\text{HCl}$ , where  $K_2[\text{HCl}]^4 = [\text{H}_2\text{O}]^2[\text{Fe}_2\text{Cl}_6]$ ; and for  $2\text{FeOCl} + \text{H}_2\text{O} = \text{Fe}_2\text{O}_3 + 2\text{HCl}$ , where  $K_3[\text{HCl}]^2 = [\text{H}_2\text{O}]$ . E. Stirnemann studied the second of these systems and obtained for  $K_2$ ,  $4.40 \times 10^{-3}$  at  $274^\circ$  or  $547^\circ \text{K.}$ , but the results at  $292^\circ$  were not satisfactory. Applying the standard equation  $\log K_2 - \log K_2 = (Q_2/R)(T_1^{-1} - T_2^{-1})$ , where  $Q_2 = 5400$  cal.,  $K_2$  is  $4.40 \times 10^{-3}$  at  $294^\circ$ , and  $2.08 \times 10^{-2}$  at  $525^\circ$   $798^\circ \text{K.}$  It also follows from known data, that  $K_1 = 8.77$  at  $525^\circ$ , when  $Q_1 = -4500$  cal.; and  $K_3 = 3.93 \times 10^{-2}$  when  $Q_3 = -9900$  cal. The relative proportions of the solid phases at different temp. are indicated in the diagram, Fig. 583. The subject was also discussed by E. Baur.

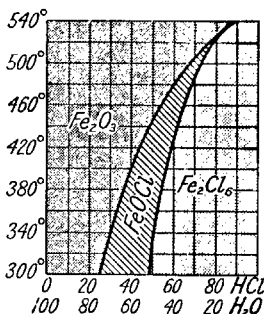


FIG. 583.—Solid Phases in the System:  $\text{FeCl}_3\text{--H}_2\text{O}$ .

R. B. Smith and P. M. Giesy obtained a continuous curve in the electrometric titration of soln. of ferric chloride with sodium hydroxide, and inferred that no oxychlorides are formed. S. Goldsztaub found the space-lattice has  $a = 3.75 \text{ \AA.}$ ,  $b = 7.95 \text{ \AA.}$ , and  $c = 3.3 \text{ \AA.}$ ; and there are two mols. per unit cell. There are two layers of Cl-atoms, with two each of alternate Fe- and O-atoms, corresponding with the perfect cleavage parallel to (010).

For the action of **hydrogen dioxide**, *vide* the iron peroxides. V. L. Bohnson represented the reaction: (i)  $2\text{FeCl}_3 + 3\text{H}_2\text{O}_2 + 2\text{H}_2\text{O} \rightleftharpoons 2\text{H}_2\text{FeO}_4 + 6\text{HCl}$ ; (ii)  $2\text{H}_2\text{FeO}_4 + 3\text{H}_2\text{O}_2 \rightleftharpoons 2\text{Fe}(\text{OH})_3 + 2\text{H}_2\text{O} + 3\text{O}_2$ ; and (iii)  $2\text{Fe}(\text{OH})_3 + 6\text{HCl} \rightleftharpoons 2\text{FeCl}_3 + 6\text{H}_2\text{O}$ , where the second reaction is measurable, and furnishes constants for a unimolecular process. V. L. Bohnson and A. C. Robertson observed that a ferric acid,  $\text{H}_2\text{FeO}_4$ , is probably formed as an intermediate product; that the temp. coeff. shows that the critical increment of the reaction is 23,960 cal., and that the frequency of the active radiation is  $2.5 \times 10^{14}$  when the wave-length is  $1.2\mu$ . E. I. Spitalsky and co-workers, I. S. Teletoff and co-workers, J. H. Walton and C. J. Christensen, W. Limanowsky, J. von Bertalan, J. Duclaux, C. S. Mummary, and A. von Kiss and F. E. Lederer also studied the reaction; and A. C. Robertson, the promotor action of cupric salts on the catalytic decomposition of hydrogen dioxide by ferric salts. H. Wieland and W. Franke studied the catalytic action of ferric salts on the decomposition of hydrogen peroxide, and found it to be less than with ferrous salts. G. Pellini and D. Meneghini observed that a well-cooled soln. of ferric chloride in anhydrous alcohol does not perceptibly influence chemically a 30 per cent. soln. of hydrogen dioxide; and the catalytic effect is very feeble. In alcoholic soln. of potassium hydroxide, and hydrogen dioxide, peroxides are formed. A. Brann, and J. H. Walton and D. O. Jones found that hydrogen dioxide reacts with an ethereal soln. of ferric chloride forming a precipitate; and with a quinoline soln. of ferric chloride, the hydrogen dioxide is vigorously decomposed. H. Kwasnik found that **barium dioxide** reacts with ferric chloride soln. in accord with  $4\text{FeCl}_3 + 6\text{BaO}_2 + 6\text{H}_2\text{O} = 3\text{O}_2 + 4\text{Fe}(\text{OH})_3 + 6\text{BaCl}_2$ .

O. Ruff, and O. Ruff and E. Ascher observed that when **fluorine** is passed over heated ferric chloride, ferric fluoride is formed. C. Friedel and J. M. Crafts said that the presence of **chlorine** hinders the dissociation of ferric chloride into ferrous chloride and chlorine at  $440^\circ$ , but W. Grünwald and V. Meyer observed no difference at  $440^\circ$ . K. H. Butler and D. McIntosh found that ferric chloride is insoluble in liquid chlorine; and J. Timmermans said that the solubility is less than 0.5 per cent. W. L. Goodwin observed that chlorine is less soluble in a soln. of ferric chloride than it is in water. M. C. Schuyten could detect no reaction between a

soln. of ferric chloride and **bromine** or **iodine**; but W. D. Bonner and H. Romeyn found that the ferric salts are reduced by iodides to the ferrous state. The reaction was studied by A. von Kiss and I. Bossanyi, and H. M. Dawson and E. Spivey. K. Schaum and W. Schleussner found that in the reaction between ferric ions and iodine the reversible photochemical reaction predominates over the Béquere effect. L. V. Pisarshevsky also studied the reaction:  $\text{Fe}^{+++} + \text{I}^- = \text{Fe}^{++} + \text{I}$ . J. Schröder observed that ferric chloride in pyridine soln. does not react with the halogens. The reaction was studied by M. Rosenberg. C. Poulenc found that gaseous **hydrogen fluoride** decomposes ferric chloride in the cold to form ferric fluoride; E. Petersen observed that **hydrofluoric acid** acts on a soln. of ferric chloride with the development of much heat. K. Fredenhagen found that ferric chloride does not dissolve in hydrofluoric acid. R. Schwarz and G. Meyer could not get dry or moist **hydrogen chloride** to unite with ferric chloride under press. and at a low temp., but hydrochloro-acids are formed when the hydrates of ferric chloride are similarly treated. R. Engel, and H. W. B. Roozeboom and F. A. H. Schreinemakers observed that when dry hydrogen chloride is passed over the hexahydrate, at ordinary temp., liquefaction occurs; and similar results were obtained with the hemiheptahydrate, the hemipentahydrate, and the dihydrate. The retardation of the hydrolysis of aq. soln. of ferric chloride by **hydrochloric acid** has been previously discussed. J. Schröder observed that ferric chloride in pyridine soln. does not react with the halide acids. The increase in the solubility of ferric chloride when hydrochloric acid is added to the soln. favours the assumption that complex hydrochloro-compounds are formed; F. G. Donnan and H. Bassett from these observations on the electrolysis of soln. of ferric chloride concluded that complex anions are formed in the hydrochloric acid soln.; E. Müller came to the same conclusion because ammonium thiocyanate does not give the characteristic red with soln. of ferric chloride in conc. hydrochloric acid; S. R. Carter and F. H. Clews, because of the fall in the oxidation potential of soln. of ferric chloride when hydrochloric acid is added; and S. R. Carter and N. J. L. Megson, because of the effect of hydrochloric acid and ferric chloride on the critical soln. temp. of isobutyric acid and water. H. W. B. Roozeboom and F. A. H. Schreinemakers' observations on the ternary system  $\text{FeCl}_3\text{-HCl-H}_2\text{O}$  indicate the existence of ferric hydrotetrachloride,  $\text{FeCl}_3\cdot\text{HCl}$ , or  $\text{HFeCl}_4$ , in the three hydrated forms di-, tetra-, and hexa-hydrates—*vide infra*; and R. Schwarz and G. Meyer's experiments on the dissociation press. show that there is a probability of the existence of **ferric hemitrihydrohemienneachloride**,  $\text{FeCl}_3\cdot 1\cdot 5\text{HCl}\cdot 4\cdot 5\text{H}_2\text{O}$ , as a green salt melting at  $-30^\circ$ ; of **ferric dihydropentachloride**,  $\text{FeCl}_3\cdot 2\text{HCl}\cdot 5\cdot 5\text{H}_2\text{O}$ , as a pale green salt melting at about  $-35^\circ$ ; of **ferric hemipentahydrohemihennachloride**,  $\text{FeCl}_3\cdot 2\cdot 5\text{HCl}\cdot 6\text{H}_2\text{O}$ , as a yellowish-green salt melting at  $-36^\circ$ ; and of yellowish-green **ferric trihydrohexachloride**,  $\text{FeCl}_3\cdot 3\text{HCl}\cdot 7\text{H}_2\text{O}$ .

According to H. W. B. Roozeboom and F. A. H. Schreinemakers, the solubilities,  $S$  mols per 100 mols of water in soln. of hydrochloric acid, are

Solid phase: $\text{Fe}_2\text{Cl}_6\cdot 12\text{H}_2\text{O}$									
		33°		20°		10°			
$S$ { HCl	:	0	5.92	0	5.60	0	8.75	16.70	
{ FeCl <sub>3</sub>	:	12.70	16.07	10	23.60	9.10	8.00	16.65	
Solid phase: $\text{Fe}_2\text{Cl}_6\cdot 7\text{H}_2\text{O}$									
		0°		-10°		-20°			
$S$ { HCl	:	0	7.52	20.40	0	20.48	0	20.56	
{ FeCl <sub>3</sub>	:	8.25	6.51	15.40	7.40	20.54	6.56	7.08	
Solid phase: $\text{Fe}_2\text{Cl}_6\cdot 7\text{H}_2\text{O}$									
		30°		20°		0°			
$S$ { HCl	:	0	4.25	0	5.6	11.05	18.05	19.50	
{ FeCl <sub>3</sub>	:	25.20	27.80	22.50	23.60	29.20	23.40	25.93	

Solid phase : $\text{Fe}_2\text{Cl}_6 \cdot 5\text{H}_2\text{O}$									
50°			40°			20°			
$S \left\{ \begin{array}{l} \text{HCl} \\ \text{FeCl}_3 \end{array} \right.$	0	3.25	0	13.40	0	11.05	11.25		
	35.00	39.95	32.40	37.45	27.90	29.20	34.25		
Solid phase : $\text{Fe}_2\text{Cl}_6 \cdot 4\text{H}_2\text{O}$									
10°			0°			-10°			
$S \left\{ \begin{array}{l} \text{HCl} \\ \text{FeCl}_3 \end{array} \right.$	17.80	24.50	24.12	36.00	24.95	26.05	27.30		
	27.75	32.75	30.04	32.16	29.60	30.50	32.05		
Solid phase : $\text{Fe}_2\text{Cl}_6$									
70°			50°			30°			
$S \left\{ \begin{array}{l} \text{HCl} \\ \text{FeCl}_3 \end{array} \right.$	0	6.75	0	21.24	17.15	31.20	33.80		
	44.00	50.00	39.92	49.33	36.75	43.49	47.80		
Solid phase : $\text{Fe}_2\text{Cl}_6$									
10°			0°			-20°			
$S \left\{ \begin{array}{l} \text{HCl} \\ \text{FeCl}_3 \end{array} \right.$	24.50	35.04	26.00	34.60	30.08	32.65			
	32.75	39.95	32.16	38.11	32.76	35.44			
Solid phase : $\text{Fe}_2\text{Cl}_6$									
45°			35°			30°			
$S \left\{ \begin{array}{l} \text{HCl} \\ \text{FeCl}_3 \end{array} \right.$	0	40.65	0	37.04	0	34.4			
	58.00	48.60	58.00	49.20	58.00	49.72			
Solid phase : $\text{Fe}_2\text{Cl}_6 \cdot 2\text{HCl} \cdot 4\text{H}_2\text{O}$									
40°			20°			0°			
$S \left\{ \begin{array}{l} \text{HCl} \\ \text{FeCl}_3 \end{array} \right.$	42.50	42.01	39.50	35.40	37.27	34.60	37.80	34.10	
	47.52	48.64	39.25	43.16	36.60	38.11	34.00	34.84	
Solid phase : $\text{Fe}_2\text{Cl}_6 \cdot 2\text{HCl} \cdot 8\text{H}_2\text{O}$									
-4.5°			-10°			-20°			
$S \left\{ \begin{array}{l} \text{HCl} \\ \text{FeCl}_3 \end{array} \right.$	20.50	23.40	20.48	31.42	19.44	34.13			
	24.50	27.40	20.54	28.53	12.10	12.90			
Solid phase : $\text{Fe}_2\text{Cl}_6 \cdot 2\text{HCl} \cdot 12\text{H}_2\text{O}$									
-10°			-15°			-20°			
$S \left\{ \begin{array}{l} \text{HCl} \\ \text{FeCl}_3 \end{array} \right.$	12.01	20.25	21.30	24.50	9.96	25.59			
	11.99	20.20	9.65	15.83	9.94	13.39			

P. Sabatier prepared **ferric hydrotetrachloride**,  $\text{FeCl}_3 \cdot \text{HCl} \cdot 2\text{H}_2\text{O}$ , or, according to A. Werner,  $[\text{Fe}(\text{H}_2\text{O})_2\text{Cl}_4]$ . The *dihydrate* was obtained by saturating hemipenta-

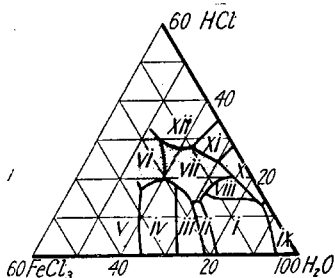


FIG. 584.—Phases in the Ternary System :  $\text{FeCl}_3$ - $\text{HCl}$ - $\text{H}_2\text{O}$ .

$\text{Fe}_2\text{Cl}_6 \cdot 5\text{H}_2\text{O}$ ; IV,  $\text{Fe}_2\text{Cl}_6 \cdot 4\text{H}_2\text{O}$ ; V,  $\text{Fe}_2\text{Cl}_6$ ; VI,  $\text{Fe}_3\text{Cl}_6 \cdot 2\text{HCl} \cdot 4\text{H}_2\text{O}$ ; VII,  $\text{Fe}_2\text{Cl}_6 \cdot 2\text{HCl} \cdot 8\text{H}_2\text{O}$ ; VIII,  $\text{Fe}_2\text{Cl}_6 \cdot 2\text{HCl} \cdot 12\text{H}_2\text{O}$ ; IX,  $\text{H}_2\text{O}$ ; X,  $\text{HCl} \cdot 3\text{H}_2\text{O}$ ; XI,  $\text{HCl} \cdot 2\text{H}_2\text{O}$ ; and XII,  $\text{HCl} \cdot \text{H}_2\text{O}$ . T. Nishimura and T. Toyama tried unsuccessfully to separate the isotopes of chlorine by converting the chlorine into hydrogen chloride, and then allowing that gas to act on hemiheptahydrated ferric chloride. The *tetrahydrate*,  $\text{FeCl}_3 \cdot \text{HCl} \cdot 4\text{H}_2\text{O}$ , or  $\text{HFeCl}_4 \cdot 4\text{H}_2\text{O}$ , was obtained by warming the hexahydrate,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , on a water-bath until it had lost two mols. of water,

and then passing hydrogen chloride over the product; and cooling the dark green liquid below  $-20^{\circ}$ . The green, columnar crystals melt at  $-3^{\circ}$ . The *hexahydrate*,  $\text{FeCl}_3 \cdot \text{HCl} \cdot 6\text{H}_2\text{O}$ , or  $\text{HFeCl}_4 \cdot 6\text{H}_2\text{O}$ , is obtained by passing hydrogen chloride over the hexahydrate,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , and cooling the liquid which is formed at  $-10^{\circ}$  to  $-20^{\circ}$ . The straw-yellow crystals melt at  $-6^{\circ}$ . If the salt be kept at its m.p. for a long time, it forms the salt  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ . M. Bobtelsky studied the catalytic action of ferric chloride on the oxidation of hydrochloric acid by chromic acid.

Ferric chloride readily reacts with many **metal fluorides** forming complex fluorides which may be precipitated, or, if the ferric chloride be in excess, they may pass into soln. The subject was studied by J. Nicklès, R. Peters, A. Byk and H. Jaffe, J. Knobloch, and L. Szebelledy. Similarly, ferric chloride unites with many **metal chlorides** forming complex salts—*vide infra*. C. F. Schönbein observed that when a mixture of anhydrous ferric chloride and **potassium bromide** is heated, bromine is evolved and potassium and ferrous chlorides are formed. J. W. Retgers, R. Peters, and N. Sasaki observed that alkali bromides react with ferric chloride soln. forming orange-yellow or deep-brown ferric bromide. F. Krauss and T. von Heidelberg noted that with boiling, sat. soln., feebly acidified, **rubidium** and **cæsium bromides** give respectively **rubidium ferric chlorobromide**, and **cæsium ferric chlorobromide**. J. M. Eder discussed the action of ferric chloride on the **silver bromide** photographic plate. C. F. Schönbein found that, even in the cold, a mixture of anhydrous ferric chloride and **potassium iodide** gives off iodine forming potassium and ferrous chlorides, and the salt liberates iodine from solid potassium or ammonium iodide. P. Schulz, and A. Naumann and P. Schulz represented the reaction of ferric chloride in acetone soln. with a soln. of potassium iodide:  $\text{FeCl}_3 + \text{KI} = \text{FeCl}_2 + \text{KCl} + \text{I}_2$ , and  $\text{FeCl}_2 + 2\text{KI} = \text{FeI}_2 + 2\text{KCl}$ . D. J. Carnegie observed that ferric chloride reacts with potassium iodide in accord with  $2\text{FeCl}_3 + 2\text{KI} = 2\text{FeCl}_2 + 2\text{KCl} + \text{I}_2$ . The reaction was studied by E. I. Orloff, L. V. Pisarshevsky, H. Tominaga and S. Toraishi, N. Sasaki, A. von Kiss, A. von Kiss and I. Bossanyi, and K. Seubert and co-workers, and they suggest that an intermediate **ferric dichloroiodide**,  $\text{FeCl}_2\text{I}$ , may be formed:  $2\text{FeCl}_2(\text{Cl}) + 2\text{KI} = 2\text{FeCl}_2\text{I} + 2\text{KCl}$ , followed by  $2\text{FeCl}_2\text{I} = 2\text{FeCl}_2 + \text{I}_2$ . The photochemical reduction was studied by S. F. Ravitz and R. G. Dickinson. The complex **potassium ferric difluotrichloride**,  $2\text{KF} \cdot \text{FeCl}_3$ , reported by P. Guyot, could not be prepared by A. Greeff. According to M. J. Gramenitzky, the oxidation of guaiacum, and the liberation of iodine from potassium iodide, by ferric chloride are much delayed if the ferric chloride soln. has been recently boiled; when kept, the cooled soln. gradually regains its original oxidizing activity. The effect may be due to diminution of the dissociated ferric chloride molecules on boiling—*vide infra*, ferrous iodide. A. Jürgens observed that the reaction between **silver iodide** and a soln. of ferric chloride is not quantitative; some iodine is liberated. A. Engelhardt represented the reaction with **lead iodide**:  $\text{PbI}_2 + 2\text{FeCl}_3 = \text{PbCl}_2 + 2\text{FeCl}_2 + \text{I}_2$ . N. M. Bell found that aq. soln. of ferric chloride decompose **bleaching powder**; with conc. soln.—e.g.,  $0.1N\text{-FeCl}_3$ —chlorine is given off, and with more dil. soln., oxygen. Ferrates may also be formed. H. Schulze found that molten **potassium chlorate** reacts vigorously with ferric chloride forming ferric oxide. M. Herschkowitsch found that when a mixture of potassium chlorate and ferric chloride is moistened, heat is developed and chlorine and chlorine dioxide are produced.

A. Vogel observed that **sulphur** does not form iron sulphide when it is heated with ferric chloride. J. B. Cammerer found that when a 3 per cent. soln. of ferric chloride is boiled with finely-divided sulphur, some gas is evolved, and about 5 per cent. of the ferric chloride is reduced; and W. Wardlaw and F. H. Clews found that when a 5 to 8 per cent. soln. of ferric chloride in hydrochloric acid is boiled with colloidal sulphur, a little sulphuric acid is formed and only about 1 per cent. of the salt is reduced. According to A. W. Ralston and J. A. Wilkinson, ferric chloride forms a yellow soln. with liquid **hydrogen sulphide**, the soln. is not stable



since a chemical reaction sets in resulting in the formation of a white precipitate. The reaction is very fast at room temp. The sp. conductivity of a sat. soln., at the temp. of the ether-carbon dioxide mixture, is  $209.9 \times 10^{-6}$  mho. J. Durocher observed that the vapour of ferric chloride reacts with hydrogen sulphide producing iron disulphide. As shown by H. Rose, and H. W. F. Wackenroder, hydrogen sulphide reduces ferric salts to ferrous salts with the deposition of sulphur, and even in the cold some sulphuric acid is formed. The reaction was studied by E. Mischke. W. Moldenhauer and E. Mischke observed that in neutral or feebly acid soln., the speed of the reduction of ferric salts by hydrogen sulphide is too large to be measured, but it is measurable in the presence of hydrochloric, sulphuric or phosphoric acid. In sulphuric acid, at  $0^\circ$  and  $20^\circ$ , and in hydrochloric, at  $0^\circ$ , it is a termolecular reaction. In hydrochloric and phosphoric acid soln., at  $20^\circ$ , it is a bimolecular reaction. In all cases, the velocity diminishes rapidly with an increase in the conc. of acid, the velocity constant being a logarithmic function of the normality of the acid. The inhibiting influence of phosphoric acid on the rate of reaction is very much greater than that of either of the other acids, and when these are added to the former they influence the velocity only to a slight extent. The inhibiting action of acids is attributed to the formation of a complex compound the nature of which also influences the order of the reaction. The precipitate of iron sulphide formed in feebly acid, neutral, or slightly alkaline soln. contains only ferrous iron, thus suggesting that the reduction proceeds with even greater rapidity than precipitation. By the action of hydrogen sulphide on freshly-precipitated ferric hydroxide, or of strongly ammoniacal ammonium sulphide on ferric sulphate soln., exactly two-thirds of the iron appears to be reduced to the ferrous state. This is probably accounted for by the formation of a **ferrous sulphoferrite**,  $4\text{FeS}, \text{Fe}_2\text{S}_3$ . A. Wassermann studied the effect of ferric chloride as catalyst on the oxidation of hydrogen sulphide by hydrogen dioxide. **Alkali sulphides** or **hydrosulphides** precipitate black iron sulphide—*vide supra*, the chemical reactions of iron. P. Schulz, and A. Naumann and P. Schulz observed that ferric chloride in acetone soln. is partially reduced by hydrogen sulphide with the separation of sulphur. J. Schröder observed that hydrogen sulphide does not act on ferric chloride in pyridine soln.; A. Schier, that with a soln. in acetonitrile, sulphur but no sulphide is precipitated; and E. Busch observed an incomplete reaction in methylal soln. P. T. Walden found that liquid **sulphur dioxide** forms a yellowish-brown soln. with anhydrous ferric chloride; which gives a deep blood-red colour with ammonium thiocyanate, and a violet-brown with salicylic acid. H. P. Cady and R. Taft observed that the ferric salt is slowly reduced to ferrous salt; and on electrolysis, a black deposit appears on the cathode, and a red one on the anode; some gas is also developed on the anode. F. Ephraim and J. Kornblum observed no sulphur dioxide gas is adsorbed by anhydrous ferric chloride. Aq. soln. of the salt are reduced to ferrous salts by sulphur dioxide, or by **alkali sulphides** or **hydrosulphites** in the presence of a little free acid; if the soln. be alkaline to litmus, the reaction is slow. J. Pinnow found that a low  $\text{H}^+$ -ion concentration favours the reduction of ferric chloride by sodium sulphite—*vide* 10. 57, 16. The reaction was studied by P. T. Austen and G. B. Hurff, T. W. Hogg, R. W. Atkinson, B. Glasmann, and A. C. Cumming and E. W. Hamilton. J. Schröder observed that sulphur dioxide does not act on ferric chloride in pyridine soln. O. Ruff and H. Einbeck found that **sulphur tetrachloride** forms **ferric sulphoheptachloride**,  $\text{FeCl}_3.\text{SCl}_4$ , in contact with ferric chloride; and the complex salt is very sensitive towards heat and moisture. According to E. Beckmann, ferric chloride dissolves in **sulphuryl chloride** to form a greenish-yellow soln. P. T. Walden found the mol. conductivity of soln. with a mol of ferric chloride in 125, 250, and 375 litres to be respectively 1.74, 2.31, and 3.01 at  $25^\circ$ . H. B. North and A. M. Hageman found that ferric chloride is readily soluble in heated **thionyl chloride**. J. Timmermans observed that ferric chloride is not soluble in **sulphur trioxide**. A. Vogel said that **sulphuric acid** produces a frothing when it acts on

ferric chloride, and hydrogen chloride is evolved: A. W. Davidson, and H. Friedrich observed that with 100 per cent. acid, yellowish-white ferric sulphate is formed. The reaction is slow in the cold, but rapid when the mixture is heated. M. Berthelot, and F. L. Browne and J. H. Mathews studied the heat developed on mixing dil. soln. of ferric chloride and dil. sulphuric acid. V. Macri found that ferric chloride soln. are instantly decolorized by dil. sulphuric acid and the colour is restored by sodium chloride. E. Pietsch and co-workers studied the reducing action of **sodium thiosulphate** on an ethereal soln. of ferric chloride; and H. Schmid, K. Jellinek and co-workers, J. Holluta and A. Martini studied the action of ferric chloride on an aq. soln. of sodium thiosulphate:  $2\text{FeCl}_3 + 2\text{Na}_2\text{S}_2\text{O}_3 = 2\text{FeCl}_2 + 2\text{NaCl} + \text{Na}_2\text{S}_4\text{O}_6$ ; and J. Mika studied the reaction by electrometric titration. H. Debus observed that aq. soln. of **trithionates, tetrathionates, pentathionates, and hexathionates** are not perceptibly changed by soln. of ferric chloride.

C. Fabr  represented the reducing action of gaseous **hydrogen selenide** on soln. of ferric chloride at ordinary temp. by  $\text{H}_2\text{Se} + 2\text{FeCl}_3 \cdot \text{Aq.} = \text{Se} + 2\text{FeCl}_2 \cdot \text{Aq.} + 2\text{HCl} \cdot \text{Aq.} + 41.94 \text{ Cals.}$  C. R. Wise observed that 100 grms. of **selenium oxydichloride** dissolve 23.40 grms. of anhydrous ferric chloride, and ferric diselenium-dioxyheptachloride,  $\text{FeCl}_3 \cdot 2\text{SeOCl}_2$ , is formed. A. P. Julien found the mol. conductivities of soln. with a mol. of ferric chloride in 1.372, 10.97, and 351.2 litres are respectively 3.164, 5.41, and 11.90 at 25°. The low value of the conductivity indicates that some complex salt is formed, and that no hydrolysis occurs. M. M. Smith and C. James observed that a precipitate is formed when **selenious acid** is added to a feebly acid soln. of ferric chloride, but if the soln. contains more than 5 per cent. of hydrochloric acid, no precipitation occurs. V. Lenher observed that **tellurium** reacts when heated with anhydrous ferric chloride in accord with  $4\text{FeCl}_3 + \text{Te} = \text{TeCl}_4 + 4\text{FeCl}_2$ ; a similar reaction occurs in aq. soln. where the reaction is reversible. M. Berthelot and C. Fabr  represented the action of **hydrogen telluride** on a soln. of ferric chloride free from oxygen by  $\text{H}_2\text{Te} + 2\text{FeCl}_3 \cdot \text{Aq.} = \text{Te} + 2\text{FeCl}_2 \cdot \text{Aq.} + 2\text{HCl} \cdot \text{Aq.} + 58.24 \text{ Cals.}$  C. A. Tibbals found that **sodium telluride** reduces an acetic acid soln. of ferric chloride to ferrous chloride with the separation of some tellurium and the formation of tellurium tetrachloride. According to W. Pethybridge, and V. Lenher, a soln. of ferric chloride extracts tellurium from the **gold-silver telluride** ores:  $(\text{Au}, \text{Ag})\text{Te}_2 + 8\text{FeCl}_3 = 2\text{TeCl}_4 + 8\text{FeCl}_2 + \text{Au}, \text{Ag.}$  The reaction is slow in the cold, rapid when heated.

Ferric chloride is not attacked by **nitrogen**. A. Guntz found that **lithium nitride** acts so vigorously on ferric chloride that it is advisable to slow down the reaction by admixed sodium chloride. Some iron nitride is formed. A. Smits observed that with **magnesium nitride**, at a high temp., some iron nitride is formed, and decomposed at the high temp. of the reaction. F. Fichter and A. Spengel observed that **aluminium nitride** acts on a boiling, 4 per cent. aq. soln. of ferric chloride forming hydrated ferric oxide, and ammonium chloride equivalent to two-thirds the nitrogen. T. Curtius and J. Rissom obtained ferric azide by the action of **sodium azide** on a soln. of ferric chloride; and L. M. Dennis and A. W. Browne obtained a red coloration on adding **silver azide** to a pyridine soln. of ferric chloride. J. N. Br nsted and K. Volqvartz studied the catalysis of nitramide by ferric ions.

The tendency of the chloride to form complexes was studied by H. Hansen. H. Buff, A. W. F. Rogstadius, C. Stahlschmidt, and G. J. Fowler noticed that a nitride is formed when ammonia acts on ferric chloride at an elevated temp. According to H. Rose, and J. Persoz, ferric chloride slowly absorbs ammonia at ordinary temp. with the evolution of a small amount of heat, and the product approximates  $\text{FeCl}_3 : \text{NH}_3$ ; but A. S. Miller showed that the reaction is vigorous, and much heat is developed so that if the current of ammonia be not conducted slowly at first, some salt may be decomposed, and ammonium chloride formed. The amount of gas absorbed at ordinary temp., say 18° to 23°, corresponds with the formation of **ferric hexamminochloride**,  $\text{FeCl}_3 \cdot 6\text{NH}_3$ . This result was confirmed by

G. F. Hüttig. C. J. Gorter studied the subject. The action of ammonia on ferric chloride was also studied by O. T. Christensen. A. S. Miller obtained the hexammine as a reddish-brown powder by the direct action of ammonia on ferric chloride, and G. F. Hüttig recommended allowing the ammonia to act on ferric chloride for 2 hrs. at room temp., then 3 hrs. at  $-79^{\circ}$ , and finally allowing the ammonia to escape at ordinary temp. and atm. press. The formation of the hexammine was found by F. Ephraim and S. Millmann to be attended by a great increase in volume. The yellowish powder was found by W. Biltz and E. Birk to have a sp. gr. of 1.54 at  $25^{\circ}/4^{\circ}$ . The hexammine is stable at room temp., in an atm. of ammonia, and when gently heated, but in a high vacuum it loses a mol. of ammonia at room temp.; A. S. Miller said that it forms a product approximating  $3\text{FeCl}_3 \cdot 2\text{NH}_3$ . F. Müller gave  $36^{\circ}$  to  $115^{\circ}$  for the dissociation temp. of the hexammine. The hexammine is insoluble in water, but H. Rose observed that his product was deliquescent in air, and dissolved in water with a hissing noise, and the formation of a dark red, transparent soln. F. Ephraim found the dissociation press. at  $27.5^{\circ}$ ,  $49^{\circ}$ ,  $65^{\circ}$ , and  $70.5^{\circ}$  to be respectively 112, 324, 586, and 714 mm. F. Müller gave  $115^{\circ}$  to  $190^{\circ}$  for the dissociation temp. of **ferric pentamminochloride**,  $\text{FeCl}_3 \cdot 5\text{NH}_3$ ;  $190^{\circ}$  to  $230^{\circ}$  for that of **ferric triamminochloride**,  $\text{FeCl}_3 \cdot 3\text{NH}_3$ ; and over  $300^{\circ}$  for the **ferric diamminochloride**,  $\text{FeCl}_3 \cdot 2\text{NH}_3$ . R. Samuel and A. R. R. Despande studied the absorption spectra of the complex chlorides. According to G. F. Hüttig, if the hexammine be placed in liquid ammonia at  $-79^{\circ}$ , it forms **ferric dodecamminochloride**,  $\text{FeCl}_3 \cdot 12\text{NH}_3$ , whose dissociation press. at  $-79^{\circ}$  is 9 mm. According to A. W. F. Rogstadius, and A. S. Miller, if ammonia acts on ferric chloride at a higher temp., reduction to ferrous chloride occurs, and ammonium chloride is formed. H. Buff, and C. Stahlschmidt found that at higher temp. some iron nitride may be formed. A. Forster and co-workers noted the formation of a precipitate when ammonia acts on an ethereal soln. of ferric chloride. P. Fireman observed that when **ammonium chloride** is melted with admixed ferric chloride a complex salt is formed, but at  $400^{\circ}$  to  $420^{\circ}$ , in a sealed tube, the reaction proceeds:  $3\text{FeCl}_3 + \text{NH}_4\text{Cl} = 3\text{FeCl}_2 + 4\text{HCl} + \text{N}$ . After 48 hrs' heating, about 95 per cent. of the theoretical yield of gas is developed. For the action of ammonia on the aq. soln. of ferric chloride, *vide infra*, the analytical reactions of iron salts. G. F. Hüttig and H. Garside passed dry ammonia into a soln. of ferric chloride in dry alcohol and obtained a yellow precipitate which rapidly darkens, and the soln. simultaneously deposits ammonium chloride. P. Schulz noticed that dry ammonia passed into an acetone soln. of ferric chloride gives a precipitate of ferric oxychloride and ammonium chloride, but no ammine is formed; an aq. soln. of ammonia precipitates hydrated ferric oxide which then dissolves in the excess of ferric chloride. J. Schröder observed that dry ammonia precipitates an insoluble complex salt from ferric chloride in pyridine soln.; E. Busch obtained a similar result with soln. in methylal. T. Curtius and F. Schrader, and H. Franzen and O. von Meyer obtained a brown precipitate on adding **hydrazine hydrate** to a soln. of ferric chloride; the precipitated **ferric hydrazine chloride** quickly passes into  $\text{FeCl}_2 \cdot 2\text{N}_2\text{H}_4$ . P. Purgotti represented the reaction with ferric salts:  $5\text{N}_2\text{H}_4 + 4\text{Fe}_2\text{O}_3 = 8\text{FeO} + 4\text{NH}_3 + 3\text{N}_2 + 4\text{H}_2\text{O}$ . A. Hantzsch and C. H. Desch observed that when **phenylhydrazine** is added to an ethereal soln. of ferric chloride, an addition product is precipitated without the evolution of a gas. L. Kahlenberg and A. T. Lincoln said that the soln. of ferric chloride in phenylhydrazine is not an electrical conductor. F. Haber showed that **hydroxylamine** oxidizes ferrous salts in alkaline soln. or in suspensions, and reduces ferric salts in acidic soln. He explained the phenomenon by assuming that hydroxylamine had two different structures,  $\text{N}_3\text{N} : \text{O}$ , and  $\text{H}_2\text{N} \cdot \text{OH}$ . A. D. Mitchell and co-workers studied the dynamics of the action of hydroxylamine on ferric salts and showed that the speed of the reaction after the early stages is directly proportional to the conc. of the hydroxylamine, to the square of that of the ferric chloride, and inversely proportional to the conc. of the ferrous salt, and to the square of the  $\text{H}^+$ -ion conc. He assumes that the

reaction is complex:  $2\text{Fe}^{++} + \text{NH}_2\text{OH} \rightleftharpoons \text{Fe}^{++} + 2\text{H}^+ + (\text{NOH}, \text{Fe}, \text{H})^{--} \rightarrow \text{N}_2\text{O}$ , etc. The temp. coeff. of the reaction is 6.5 for  $10^\circ$ . The speed of the reaction is depressed by the addition of neutral salts. E. Ehler and E. Schott found that with a 5 per cent. soln. of hydroxylamine in a soln. of ferric chloride in absolute alcohol, at  $-18^\circ$ , a brown precipitate containing hydroxylamine is deposited—probably **ferric hydroxylaminochloride**. R. Weber observed that **nitric oxide** acts on ferric chloride, and A. Besson obtained two products—a yellow powder at a low temp., and a brown product at a high temp. V. Thomas showed that with dry ferric chloride and dry nitric oxide, **ferric heminitrosylchloride**,  $2\text{FeCl}_3 \cdot \text{NO}$ , is formed as a yellowish-brown powder; if the temp. approaches  $60^\circ$ , dark red **ferric tetranitrosylchloride**,  $4\text{FeCl}_3 \cdot \text{NO}$ , is formed—*vide* 8. 49, 35. W. Manchot studied soln. of nitric oxide in alcoholic soln. of ferric chloride. A. Besson observed that at room temp., ferric chloride absorbs **nitrogen peroxide** gas, forming a compound which, according to V. Thomas, is **ferric nitroxylchloride**,  $\text{FeCl}_3 \cdot \text{NO}_2$ . At a higher temp., ferric oxide is formed. P. F. Frankland and R. C. Farmer found that the dry salt is insoluble in and not attacked by liquid nitrogen peroxide, but if traces of moisture be present, the salt is rapidly attacked and dissolved. V. Thomas, and I. Bellucci studied the action of nitric oxide on an ethereal soln. of ferric chloride, and found that ferrous chloride is formed; if some water be also present, the reaction is symbolized:  $3\text{Fe}^{++} + \text{NO} + 2\text{H}_2\text{O} \rightleftharpoons 3\text{Fe}^{++} + \text{NO}_3' + 4\text{H}^+$ . W. Manchot found that nitric oxide partially reduces the ferric chloride in soln. in acetone to ferrous chloride. R. Weber observed that if ferric chloride be warmed in the vapour of **nitrosyl chloride**, a complex salt is formed; H. Rheinboldt and R. Wasserfuhr observed that the clear, dark red liquid formed by the action of dry nitrosyl chloride vapour on dry ferric chloride at room temp., furnishes **ferric nitrosyl tetrachloride**,  $\text{FeCl}_3 \cdot \text{NOCl}$ , when the excess of nitrosyl chloride is evaporated off. The complex salt was studied by R. Weber, J. J. Sudborough, H. Gall and H. Mengdehl, and W. J. van Heteren. Dry ferric chloride was found by W. J. van Heteren to be soluble in liquid nitrosyl chloride forming ferric nitrosyl tetrachloride. L. Pesci represented the reaction of **potassium nitrite** on a soln. of ferric chloride by the equation:  $2\text{FeCl}_3 + 6\text{KNO}_2 + 2\text{H}_2\text{O} = 2\text{FeO}(\text{OH}) + 6\text{KCl} + 2\text{HNO}_3 + 4\text{NO}$ ; and J. Matuschek, the reaction with **sodium nitrite** by  $2\text{FeCl}_3 + 6\text{NaNO}_2 = 2\text{Fe}(\text{NO}_2)_3 + 6\text{NaCl}$ , followed by  $2\text{Fe}(\text{NO}_2)_3 + 3\text{H}_2\text{O} = 2\text{Fe}(\text{OH})_3 + 3\text{NO}_2 + 3\text{NO}$ ; he also found that a suspension of the hexahydrate in carbon disulphide reacts with sodium nitrite forming nitric oxide which escapes, and nitrogen peroxide which dissolves in the carbon disulphide. H. Wurtz observed that the repeated evaporation of a soln. of ferric chloride with **nitric acid**, mixed with a little potassium chlorate, ultimately yields ferric nitrate free from chlorine. V. Macri found that the soln. is decolorized by dil. nitric acid, and that the colour is restored by sodium chloride.

J. H. Gladstone observed that **phosphorus** acts on anhydrous ferric chloride forming phosphorus trichloride; and A. Granger added that at a dull red-heat, iron phosphide,  $\text{Fe}_2\text{P}_3$ , is formed. L. Rosenstein found that red phosphorus when boiled with an acidified soln. of ferric chloride rapidly reduces it quantitatively to ferrous chloride. H. Rose found that when **phosphine** acts on dry ferric chloride in the cold, hydrogen chloride is evolved and iron phosphide is formed; and P. Kulisch showed that in aq. soln., phosphoric acid and ferrous chloride are produced. R. Weber, and A. E. Baudrimont found that **phosphorus pentachloride** reacts with ferric chloride furnishing dark brown **ferric phosphochloride**,  $\text{FeCl}_3 \cdot \text{PCl}_5$ , melting at about  $98^\circ$ , and boiling above  $280^\circ$ ; the salt is decomposed by water or moist air. A. W. Cronander studied this compound. P. T. Walden found that ferric chloride is slightly soluble in **phosphorus trichloride**—L. Kahlenberg and A. T. Lincoln said insoluble—and soluble in **phosphorus tribromide**, as well as in **phosphoryl chloride**. H. P. Cady and R. Taft said that the soln. in phosphoryl chloride becomes gelatinous in a few months; and when the soln. is electrolyzed, a black deposit appears on the cathode. G. Oddo said that soln. of 0.5307, 1.8426,

and 2.8633 grms. of ferric chloride in 100 grms. of phosphoryl chloride lower the f.p. respectively  $0.575^{\circ}$ ,  $0.942^{\circ}$ , and  $1.548^{\circ}$ . O. Ruff and H. Einbeck obtained yellow, crystalline **ferric hemiphosphorylchloride**,  $2\text{FeCl}_3 \cdot \text{POCl}_3$ . C. Reinhardt observed that a warm soln. of ferric chloride is rapidly reduced by **sodium hypophosphite**; T. Salzer obtained a white precipitate on adding **hypophosphorous acid** to a soln. of ferric chloride; and C. Reinhardt found that a hydrochloric acid soln. of ferric chloride is decolorized by **phosphoric acid** owing to the formation of a ferric phosphate. V. Macri studied the action of phosphoric acid. E. Glatzel represented the reaction with **phosphorus pentasulphide**:  $6\text{FeCl}_3 + 2\text{P}_2\text{S}_5 = 3\text{FeCl}_2 + 3\text{FeS}_2 + 4\text{PSCl}_3$ .

According to J. Napier, H. Schild, and L. Kahlenberg and J. V. Steinle, **arsenic** dissolves in an aq. soln. of ferric chloride, and ferrous chloride is formed:  $6\text{FeCl}_3 + 2\text{As} + 3\text{H}_2\text{O} = \text{As}_2\text{O}_3 + 6\text{FeCl}_2 + 6\text{HCl}$ . P. Schulz said that arsenic does not act on ferric chloride in acetone soln., and J. Schröder observed that ferric chloride is reduced to ferrous chloride in pyridine soln. R. Napoli represented the action of **arsine** on a soln. of ferric chloride by  $3\text{FeCl}_3 + \text{AsH}_3 = 3\text{FeCl}_2 + \text{AsCl}_3 + \frac{3}{2}\text{H}_2$ , and the arsenic trichloride is hydrolyzed to arsenious acid. The reaction with arsine is slow in neutral soln., but more rapid in acidic soln., but it is not quantitative. H. Reckleben and co-workers said that the **arsenious acid** is oxidized to arsenic acid. C. F. Schönbein found that **arsenic trioxide** intensified the colour of a dil. aq. soln. of ferric chloride. L. Winogradoff, and K. Jellinek and L. Winogradoff observed that ferric chloride is reduced by **arsenious acid**:  $2\text{FeCl}_3 + \text{H}_3\text{AsO}_3 + \text{H}_2\text{O} \rightleftharpoons 2\text{FeCl}_2 + \text{H}_3\text{AsO}_4 + 2\text{HCl}$  in the presence of 1.5*N*- to 4*N*-HCl, at  $107^{\circ}$  to  $127^{\circ}$ , in sealed tubes. At  $107^{\circ}$ , the constant  $[\text{H}_3\text{AsO}_3] \cdot [\text{FeCl}_3]^2 / [\text{H}_3\text{AsO}_4] \cdot [\text{FeCl}_2]^2 \cdot [\text{HCl}]^2$  is  $3.54 \times 10^{-2}$ ; at  $127^{\circ}$ , it is  $1.17 \times 10^{-1}$ . The thermal value of the ( $\rightarrow$ ) reaction is +18,000 cal. Both reactions appear to be termolecular, and are strongly catalyzed by hydrochloric acid. The kinetics of the reaction were studied by J. C. Sarma. P. T. Walden found that **arsenic trichloride** dissolves ferric chloride forming a yellow soln. which, according to L. Kahlenberg and A. T. Lincoln, is a good electrical conductor. P. T. Walden also found that ferric chloride is sparingly soluble in **arsenic tribromide**; the soln. with a mol of ferric chloride per 100 litres has a mol. conductivity of 1.325 at  $33^{\circ}$ ; the lowering of the f.p. of a 0.129 per cent. soln. is  $0.170^{\circ}$ . These results being different from what are obtained with soln. of other substances in this solvent are attributed to a chemical reaction between solvent and solute. T. Rieckher found that when **arsenic sulphide** is boiled with a soln. of ferric chloride, arsenic chloride is formed and volatilized quantitatively, and J. B. Cammerer represented the reaction with a 3 per cent. soln. of ferric chloride:  $\text{As}_2\text{S}_3 + 10\text{FeCl}_3 + 5\text{H}_2\text{O} = \text{As}_2\text{O}_5 + 10\text{FeCl}_2 + 10\text{HCl} + 3\text{S}$ , only traces of sulphuric acid and arsenious acid are formed. J. Napier observed that a hot, neutral or feebly acidic, conc. soln. of ferric chloride attacks **antimony**, forming ferrous and antimonous chlorides; and analogous results were obtained by J. Attfield, T. Rieckher, H. Schild, and N. Welwart. P. Schulz said that antimony slowly reduces ferric to ferrous chloride in acetone soln., and J. Schröder obtained a similar result in pyridine soln. S. Tolloczko found that ferric chloride forms a brown soln. with **antimony trichloride**. R. F. Weinland and H. Schmid obtained a complex with **antimony pentachloride**, namely, **antimony ferric octochloride**,  $\text{SbCl}_5 \cdot \text{FeCl}_3 \cdot 8\text{H}_2\text{O}$ . W. Lindner, and T. Rieckher found that powdered **antimony sulphide** is easily attacked by a boiling, feebly acidic soln. of ferric chloride:  $6\text{FeCl}_3 + \text{Sb}_2\text{S}_3 = 6\text{FeCl}_2 + 2\text{SbCl}_3 + 3\text{S}$ . J. B. Cammerer said that with a 3 per cent. soln. of ferric chloride some antimony oxychloride is formed. D. J. Carnegie added that antimony sulphide does not reduce ferric chloride soln. According to J. Napier, **bismuth** readily dissolves in a soln. of ferric chloride, with a quantitative reduction to ferrous chloride, and the formation of bismuth chloride:  $\text{Bi} + 3\text{FeCl}_3 = \text{BiCl}_3 + 3\text{FeCl}_2$ . H. Schild, A. Kurtenacker and F. Werner, and W. Strecker and A. Herrmann obtained confirmatory results; and P. Schulz said that bismuth slowly reduces ferric to ferrous

chloride in acetone soln., and J. Schröder obtained a similar result in pyridine soln. K. Someya observed that the reduction is quantitative with **bismuth amalgam**. J. Aloy studied the action of **bismuth trioxide**, on the soln. of ferric chloride. G. Herrmann observed that ferric chloride and **bismuth chloride** have a eutectic at 171.5° and 23 per cent. of ferric chloride, Fig. 585, but no compound is formed. J. B. Cammerer found that the reaction with **bismuth sulphide** resembles that with antimony sulphide.

According to C. F. Schönbein, and E. Heymann and co-workers, when a soln. of ferric chloride is shaken up with powdered **carbon**, it is reduced to ferrous chloride; the action is quicker the finer is the grain-size of the carbon. Wood charcoal and lamp-black act faster than sugar charcoal. Powdered coke acts similarly. Washing the powdered coke with hydrochloric acid and water was found by

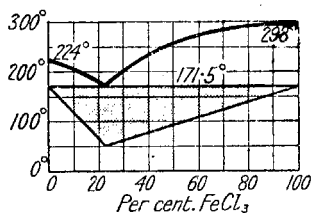


Fig. 585.—Freezing-point Curves of the Binary System:  $\text{BiCl}_3\text{--FeCl}_3$ .

A. Tingle to reduce its activity. N. Schiloff and B. Nekrassoff studied this subject. V. S. Krym and S. J. Pantschenko, and G. Stadnikoff and N. F. Proskurnina examined the reducing action of coke, coal, anthracite, and lignite. The reaction is represented:  $4\text{FeCl}_3 + 2\text{H}_2\text{O} + \text{C} = 4\text{FeCl}_2 + 4\text{HCl} + \text{CO}_2$ . E. Heymann found the reducing value, expressed in milligram atoms of iron per gram of carbon or wood charcoal purified by hydrochloric acid and water, is 0.75, and when the charcoal is de-gassed at 800° in vacuo for 3 days, 1.48; Ceylon graphite washed with hydrochloric acid and water, and de-gassed at 300°, 0.007; Acheson graphite, similarly treated, 0.007; carbonized hæmoglobin heated 5 hrs. in vacuo at 800°, 0.79; and carbon obtained from carbon tetrachloride, 1.23 to 1.40. The adsorption of ferric chloride from aq. soln. by carbon was studied by A. Tingle, E. Heymann and co-workers, N. Schiloff and L. Lepin, II. Leunig, N. Schiloff, D. J. W. Kreulen, T. Sabalitschka and W. Erdmann, and A. W. Thomas and T. R. le Compte; and from its soln. in acetone, and ethyl acetate, by W. F. O. de Coninck. The reducing action of animal charcoal was studied by W. Heintz, W. F. O. de Coninck, and R. Kuhn and A. Wassermann. E. Baur and A. Rebmann studied the effect of ferric chloride on the photolysis of **carbon dioxide**; and W. Mang, the action of **thiocarbonates**. W. Manchot and co-workers found that soln. of 0, 13.433, and 21.558 grms. of  $\text{FeCl}_3$  per 100 c.c. dissolve, respectively, 95.7, 63.0, and 51.6 c.c. of **acetylene** at 25°. L. Kahlenberg and A. T. Lincoln found that ferric chloride is soluble in **heptane**, **amylene**, **toluene**, **menthene**, **xylene**, and **cymene**, and that the soln. do not conduct the electric current. R. Schmalz said that ferric chloride is insoluble in **cyclohexane**. J. Timmermans observed that **benzoyl-p-xylene** dissolves less than 0.5 per cent. of ferric chloride. R. Colley, and E. Busch observed that ferric chloride is sparingly soluble in **benzene**, forming a yellow soln. which becomes brown. L. Kahlenberg and A. T. Lincoln said that the soln. is a poor electric conductor. J. Timmermans observed that ferric chloride is soluble in **ethylbenzene**, and in **naphthalene**.

The complex with **trimethylethylene** was studied by W. C. Gangloff and W. E. Henderson; with **stilbene**, and with **diphenylbutadiene**, by H. von Euler and H. Willstädt. M. C. Boswell and R. R. McLaughlin observed that in Friedel-Crafts' reaction, the presence of ferric chloride stimulates the catalytic action of aluminium chloride although ferric chloride alone has only one-third the activity of aluminium chloride—a subject studied by W. A. Riddell and C. R. Noller. J. Timmermans observed that the solubility of ferric chloride in **methyl chloride** is less than 0.5 per cent., likewise **methyl bromide**, and in **ethyl chloride** and **bromide**; it is soluble in **methylene chloride**; and **chloroform** dissolves over 0.5 per cent.  $\text{FeCl}_3$ . E. Busch said that the soln. in chloroform is yellow which, with time, changes to brown. K. Ott studied the reaction between ferric chloride in chloroform soln. and benzyl sulphide. L. Kahlenberg and A. T. Lincoln observed

that soln. of ferric chloride in chloroform, and **carbon tetrachloride** are non-conducting; J. Timmermans said that the salt is insoluble in carbon tetrachloride; and that **bromoform** dissolves over 0.5 per cent.  $\text{FeCl}_3$ . K. Ott observed that the salt is soluble in **acetylene tetrachloride**, **ethylene trichloride**, and **ethylene dichloride**. L. Kahlenberg and A. T. Lincoln found that soln. of ferric chloride in **ethylene chloride** and **bromide** are non-conducting; likewise also are soln. in **methylene iodide**, in **trichlorobenzene**, in **bromobenzene**, in **benzyl chloride**, and in **benzal chloride**. Soln. of ferric chloride in **acetyl chloride** were found by L. Kahlenberg and A. T. Lincoln, and L. I. Shaw to be good conductors, likewise also soln. in **benzoyl chloride**, whilst soln. in **epichlorhydrin** are fair conductors. The complex salt with benzoyl chloride was studied by M. Nencki, and J. Boeseken. The complex with **phenyl bis-methylchloride** was studied by M. Gomberg and L. H. Cone; with **phenyl tris-methylchloride**, with **phenyl-bromotrismethyl chloride**, and with **phenyl-iodo-trismethylchloride**, by A. Bayer and H. Aickelin; **tri-*p*-tolylchloromethane**, by M. Gomberg; with the **phenylpyrylium chlorides**, by W. Dilthey; with the **benzopyrylium chlorides**, by H. Decker and co-workers, W. Dilthey, W. Borsche and K. Wunder, and W. H. Perkin and co-workers; with **naphthopyrylium chloride**, by H. Decker and co-workers, and R. Fosse and L. Lesage; with **xanthylium chlorides**, by H. Decker and co-workers, A. Werner, M. Gomberg and L. H. Cone, M. Gomberg and C. J. West, L. H. Cone and C. J. West, F. Kehrmann and J. Knop, and J. von Braun and E. Aust; with **coeroxonium chloride**, by H. Decker and co-workers; with **benzocoeroxonium chloride**, by E. Laube, and H. Decker and E. Laube; with **coerbioxonium chloride**, by H. Decker and co-workers; with **tribenzylsulphonium chloride**, and cyanide, by A. Forster and co-workers, and K. A. Hofmann and K. Ott; with **methylthioxanthylium chloride**, by H. Decker and co-workers; with **coerthonium chloride**, and **methylcoerthonium chloride**, by H. Decker and co-workers; with **coerbithonium chloride**, and **dimethylcoerbithonium chloride**, by H. Decker and co-workers; with **thianthrene-dithonium chloride** and **methoxythianthrenedithonium chloride**, by K. Fries and co-workers; and with various **phenazthonium chlorides**, by F. Kehrmann and L. Schild, R. Mitsugi and co-workers, and R. Möhlau and co-workers. Soln. in **methyl or ethyl sulphide** were found by J. Timmermans to dissolve more than 0.5 per cent. of  $\text{FeCl}_3$ ; P. C. Ray and P. C. Mukherjee discussed complexes with ethyl sulphide,  $\text{H}[\text{FeCl}_4(\text{C}_4\text{H}_{10}\text{S})(\text{H}_2\text{O})]$ , and with methylene sulphide,  $\text{HFeCl}_4(\text{C}_2\text{H}_4\text{S})_2 \cdot 4\text{H}_2\text{O}$ . The complex with **benzyl sulphide** was studied by A. Forster and co-workers; with ***p*-tolylsulphoxide**, by K. A. Hofmann and K. Ott; and with **tribenzylphosphine oxide**, by F. Fleissner. A. Benrath observed a reaction with **trioxymethylene** occurs in benzene soln.

G. Gore said that a soln. of ferric chloride is not reduced by **carbon monoxide** admixed with the dioxide. A. Mittasch found that ferric chloride is almost insoluble in **nickel carbonyl**. J. Timmermans said that ferric chloride is insoluble in **carbon disulphide**; but H. Arctowsky, and E. Busch said that it forms a pale yellow soln. L. Klein, and H. Stolzenberg observed that anhydrous ferric chloride unites with **hydrogen cyanide** with a hissing noise, and then dissolves in an excess of the solvent. When the excess of solvent is evaporated, there remain brownish-red crystals of ferric dihydrocyanidochloride,  $\text{FeCl}_3 \cdot 2\text{HCN}$ . The complex was studied by L. Klein. L. Kahlenberg and H. Schlundt found the mol. conductivities of soln. with a mol of ferric chloride in 4.17, 33.12, 431.1, and 1042.0 litres of solvent to be respectively 111.7, 154.0, 213.7, and 259.9. Observations were also made by K. Fredenhagen and J. Dahmlos. E. Pietsch and co-workers studied the action of **potassium ferrocyanide** on ferric chloride in ethereal soln. L. Klein found that **cyanogen chloride** is taken up by ferric chloride with the evolution of heat. J. H. Gladstone, G. Magnanini, J. Clarens, and G. Krüss and H. Moraht studied the reversible reaction with **thiocyanates**:  $\text{FeCl}_3 + 3\text{KCys} \rightleftharpoons \text{Fe}(\text{Cys})_3 + 3\text{KCl}$ . A. K. Bhattacharya and N. R. Dhar found that the reaction with potassium thiocyanate is favoured by light of wave-length 8500 Å. K. C. Bailey observed

that in the extraction of soln. of potassium thiocyanate and ferric chloride with ether, in the case where the thiocyanate predominates, and where the colour is paler, the ether extracts practically pure thiocyanate, whilst when the ferric chloride is in excess and the soln. is sufficiently concentrated to impart some colour to the ether, hydrochloric acid formed by hydrolysis of ferric chloride liberates thiocyanic acid, and the extract contains both ferric chloride and thiocyanic acid. In H. Lachs and H. Friedenthal's process the extraction of small quantities of iron with ether becomes progressively more difficult as the proportion of iron in the soln. is reduced. K. C. Bailey and J. D. Kidd found the f.p. curve of potassium thiocyanate and ferric chloride does not have breaks indicative of the formation of complex salts. J. F. Durand and K. C. Bailey studied the reaction with silver thiocyanate. J. Clarens said that the thiocyanic acid liberated in acidic soln. does not react with ferric chloride but is slowly polymerized. E. Schaer observed that the reaction with thiocyanates is more sensitive in alcoholic than in aq. soln. J. Schröder obtained red colorations with silver and potassium thiocyanates and a pyridine soln. of ferric chloride; and with ammonium thiocyanate, ammonium chloride is also precipitated. A. Schier observed blood-red colorations are produced by thiocyanates in soln. of ferric chloride in acetonitrile. K. A. Hofmann and co-workers found that dry **ferrous cyanide** in a soln. of ferric chloride in dry alcohol gave a dark blue precipitate.

E. Lloyd and co-workers gave for the solubility of anhydrous ferric chloride in **methyl alcohol** at 0°, 15°, and 30°, respectively 1.31, 1.43, and 1.61. According to A. Benrath, ferric chloride in methyl alcohol soln. is rapidly reduced to ferrous chloride, on exposure to sunlight. The light supplies the energy necessary for the formation of aldehyde, etc., as products of primary reaction:  $2\text{FeCl}_3 + \text{CH}_3\text{OH} = 2\text{FeCl}_2 + \text{H.CO.H} + 2\text{HCl}$ , and  $2\text{FeCl}_3 + \text{C}_2\text{H}_5\text{OH} = 2\text{FeCl}_2 + \text{CH}_3\text{CO.H} + 2\text{HCl}$ ; conc. soln. deposit crystals of  $\text{FeCl}_2 \cdot 4\text{CH}_3\text{OH}$ , and if any water is present crystals of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  are formed. Observations were also made by W. F. O. de Coninck. F. Kuhlmann examined the action of heat on the soln., and E. Lloyd and co-workers found that when the alcoholic soln. is warmed above 50° for a long time, chloroform and a red precipitate are produced; if the soln. is boiling, hydrogen chloride is evolved. Ferric chloride is soluble in **ethyl alcohol**; likewise also the hydrates, as observed by G. C. Wittstein; and, according to F. L. Winckler, the soln. in 96 per cent. alcohol remains liquid when cooled to -7.5°, but when stirred with a glass rod, the yellow liquid solidifies, and the temp. rises to 19°. W. Schnellbach and J. Rosin found that 100 grms. of ethyl alcohol dissolve 51.45 grms. of ferric chloride. M. Prasad and P. S. Limaye studied the photochemical reduction of the alcoholic soln. E. Lloyd and co-workers observed that **ferric diethylalcohol chloride**,  $\text{FeCl}_3 \cdot 2\text{C}_2\text{H}_5\text{OH}$ , is formed, and the domain of existence is indicated in Fig. 586. The solubility, *S* grms. of  $\text{FeCl}_3$  per gram of dry alcohol, is:

	0°	15°	30°	40°	50°	40°	30°	20.6°	30°	40°
<i>S</i>	1.36	1.41	1.49	1.55	1.76	1.87	1.94	1.99	2.03	2.07
	$\text{FeCl}_3 \cdot 2\text{C}_2\text{H}_5\text{OH}$							$\text{FeCl}_3$		

The results are plotted in Fig. 586; there is a eutectic at 20.6°; and the m.p. of the complex,  $\text{FeCl}_3 \cdot 2\text{C}_2\text{H}_5\text{OH}$ , is about 50°. The raising of the b.p. of the alcoholic soln. was found by P. T. Müller, and E. Beckmann to be in harmony with the assumption that the mol. of the solute is  $\text{FeCl}_3$ . E. Lloyd and co-workers found that when the soln. is kept at a temp. over 50° for some time, chloroform and a red precipitate are formed as in the case of methyl alcohol; the boiling soln. gives off hydrogen chloride. H. J. H. Fenton, and J. H. Walton and C. J. Christensen studied the oxidation of alcohol by hydrogen dioxide with ferrous or ferric salts as catalysts. R. Phillips, W. F. O. de Coninck, and H. Mosler observed that a soln. of ferric chloride in ethyl alcohol is hydrolyzed with the separation of hydrated ferric oxide; the hydrolysis does not proceed so readily as in aq. soln. The tincture *tonico-nervina*, mentioned in connection with the history of the iron



chlorides, was a soln. of ferric chloride in alcohol, and it was known to the early chemists that the liquid was decolorized by exposure to light, and that the golden-yellow colour of the soln. was restored in darkness—but, according to T. von Grotthuss, not completely. The reaction was studied by J. Fiedler, and G. Kerner.

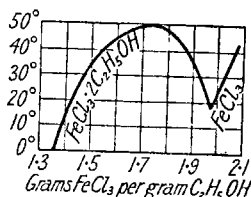


FIG. 586.—The Solubility of Ferric Chloride in Ethyl Alcohol.

A. Benrath's observations on the action of light on the soln. are indicated in connection with soln. in methyl alcohol; the subject was also investigated by E. Puxeddu. Observations on the magnetic susceptibility, and electrical conductivity of soln. in methyl, ethyl, **isobutyl**, **isoamyl**, **allyl**, and **benzyl alcohols**, **glycol**, and **glycerol**, are indicated above. M. Prasad and N. V. Sohoni studied the photochemical decomposition of soln. in ethyl, propyl, butyl, and amyl alcohols. The physical and chemical properties of these soln. are also discussed above. L. Kahlenberg and

A. T. Lincoln observed that ferric chloride is soluble in **phenol**, and in *m*-**cresol**, and the soln. are electrically a conductor; the solubility in phenol was found by J. Timmermans to exceed 0.5 per cent., and likewise with **phenetol**, and **anethol**, whilst L. Kahlenberg and A. T. Lincoln observed that the soln. in **anisol** is electrically a conductor. The absorption spectra of soln. of ferric chloride and phenol were investigated by E. F. Wesp and W. R. Boode. T. Pavolini studied the action of the salt on **phenol oxide**; and J. V. Dubsky and co-workers, on **glycocoll**; and K. Kimura and H. Sueda, on **dimethylglyoxime**.

A. F. Gehlen said that anhydrous ferric chloride dissolves in **ether** with the evolution of heat; H. E. Williams, that the hexahydrate dissolves in dry ether; G. C. Wittstein, that the hemiheptahydrate dissolves in ether; and E. Pinerua, that it similarly dissolves in ether saturated with hydrogen chloride. J. W. Rothe observed that some of the ether is decomposed, and E. Busch noted that the soln. at first yellow soon becomes dark brown. When the ethereal soln. is evaporated, A. Forster and co-workers observed that ferric chloride is decomposed. E. Beckmann, P. T. Müller, and R. Lespieau studied the mol. wt. of the salt from the effect on the b.p. of ether, and found results in agreement with  $\text{FeCl}_3$  for dil. soln., and in conc. soln. a partial polymerization to  $\text{Fe}_2\text{Cl}_6$ . According to A. Vogel, ferric chloride is perceptibly volatile from an ethereal soln. even at temp. below  $30^\circ$ , but H. P. Talbot said that the volatility cannot be greater since the ether distilled from the soln. on a water-bath contains only traces of iron. This trace may have been mechanically carried over, and not the result of volatility—*vide supra*, the volatility of ferric chloride. F. Mylius and C. Huttner noted that the ethereal soln. suffers some decomposition at a higher temp. A. F. Gehlen observed that when an ethereal soln. of ferric chloride is decomposed by exposure to light, the ferric chloride is reduced to the ferrous salt; and observations on the subject were made by F. Jahn, A. Benrath, L. E. Jonas, and J. W. Rothe. P. Chastaing studied the relation between the rate of the reduction and the wave-length of the light—violet light is the most active, whilst yellow light and red light act very slowly. E. Puxeddu, and E. Puxeddu and F. L. Vodret found that the change occurs more slowly in arc-light than in sunlight, and they showed that some chlorine is consumed in chlorinating the ether so that the reaction is not reversible in the dark. Conc. ethereal soln. yield ferrous chloride and a black organic compound containing iron. Up to a certain stage of progress, the reaction appears unimolecular. One form of the *tinctura tonico-nervina*, mentioned above, was a soln. of ferric chloride in a mixture of alcohol and ether, and it was known to T. von Grotthuss, E. L. Schubarth, G. Suckow, and A. F. Gehlen that it forms ferrous chloride on exposure to sunlight, and some ethyl chloride is produced at the same time. J. Fiedler studied the reaction. E. G. Thorin found that ether is less soluble in 0.5N- $\text{FeCl}_3$  than it is in water; and F. N. Speller that ether is less soluble in a hydrochloric acid soln. of ferric chloride than it is in aq. hydrochloric acid

alone. He found that *S* c.c. of ether are dissolved by 100 c.c. of aq. hydrochloric acid with ferric chloride in soln. at 16° to 19°:

Sp. gr. HCl	1-177	1-140	1-123	1-115	1-093	1-075	1-055
<i>S</i>	139	71-5	43-3	35	21-5	16	12

W. Skey proposed to separate ferric chloride from many associated chlorides by shaking the aq. soln. with ether. Two layers are formed—an ethereal soln. of ferric chloride, and an aq. soln. of other chlorides below. The process was examined by J. W. Rothe, M. Hanriot, and J. W. Mellor. F. Mylius and C. Hüttner, and N. de Kolossowsky studied the distribution of ferric chloride between water and ethyl ether at 18°; and F. N. Speller found that when a gram of iron as ferric chloride is dissolved in 100 c.c. of aqueous hydrochloric acid of different concentrations, at 18°, and shaken with 100 c.c. of ether, the distribution of the ferric chloride between the two layers is as follows:

Sp. gr. HCl	1-193	1-158	1-151	1-123	1-111	1-103	1-0825	1-06	1-0424
Fe <sub>3</sub> Aq.	99-0	92-84	74-0	7-2	2-0	1-95	10-0	87-0	99-6 per cent.
{ Ether	1-0	7-16	26-0	92-8	98-0	98-05	90-0	13-0	0-4 „

The complex with ethyl ether was studied by A. Forster and co-workers. R. Phillips observed that the presence of **sugar** in the aq. soln. hinders the hydrolysis of ferric chloride; and R. M. Purkayastha studied the reduction of ferric chloride by sugars. A. Dumansky and L. G. Krapiwina studied the ternary system:  $\text{FeCl}_3\text{-H}_2\text{O-sugar}$ . A. Benrath found that ferric chloride dissolves in **formaldehyde**, and the soln. is decomposed with the formation of ferrous chloride in light, and when heated. L. Kahlenberg and A. T. Lincoln noted that ferric chloride dissolves in **acetaldehyde** with the development of heat, and, according to A. Benrath, this liquid forms a black, spongy mass. C. Dufraisse and R. Horclois studied the catalytic action of ferric chloride on various organic compounds. L. Kahlenberg and A. T. Lincoln observed that ferric chloride is soluble in **chloral**, but the soln. is non-conducting; and it is also soluble in **paraldehyde**, and the soln. is a good electrical conductor, as observed by L. Kahlenberg and A. T. Lincoln—*vide supra*; the salt is soluble in **cinnamic aldehyde**, and the soln. is a fair electrical conductor. P. T. Walden found that **benzaldehyde** forms a brown soln. with ferric chloride, and observations on the electrical conductivity (*q.v.*) were made by P. T. Walden, and L. Kahlenberg and A. T. Lincoln. E. Raymond studied the catalytic oxidation. L. I. Shaw found the soln. of ferric chloride in **salicylaldehyde** is a good conductor (*q.v.*), and observations were made by L. Kahlenberg and A. T. Lincoln, and A. T. Lincoln. Similar observations were made with respect to soln. in **furfural**. W. C. Gangloff and W. E. Henderson studied the complex with **furfuraldehyde**. W. Eidmann observed that ferric chloride is soluble in **acetone**; and P. Schulz, and A. Naumann and P. Schulz added that a gram of the  $\text{FeCl}_3$  dissolves in 1-5888 grms. of acetone at 18°, and the sp. gr. is 1-1603. The soln. were studied by W. H. Krug and K. P. McElroy. J. Timmermans observed that the soln. decomposes on keeping and deposits a precipitate; P. Schulz added that with the purified acetone, much of the ferric chloride is reduced to ferrous chloride, but if the acetone be sat. with hydrogen chloride, no reduction occurs. W. F. O. de Coninck observed that a very dil. soln. is stable in light, but not so if traces of methyl alcohol are present. The soln. are rapidly decolorized when filtered through animal charcoal. The soln. with some methyl alcohol, unlike the soln. with purified acetone above, gives a precipitate with silver nitrate after filtration through the charcoal. This is the result of a partial decomposition of the acetone soln. containing the methyl alcohol. L. Kahlenberg and A. T. Lincoln, and A. T. Lincoln found that ferric chloride is soluble in **methylpropylketone**, and the soln. is electrically conducting (*q.v.*); likewise with soln. in **acetophenone**. J. Timmermans observed that **benzophenone** dissolves more than 0-5 per cent. of ferric chloride. The complex with benzophenone was studied by J. Boeseken; with **phenyl-cyclopentene**, by W. Borsche and W. Menz; with **dibenzalacetone**, by F. Straus, and A. Rosenheim and W. Levy;

with **cinnamylideneacetophenone**, and **dicinnamylideneacetone**, by A. Rosenheim and W. Levy; with **phenanthrenequinone**, by K. H. Meyer; with **2,4-dimethoxy-*w*-oxybenzalacetophenone**, by W. H. Perkin and co-workers; with **dimethylchromone** and **dimethylthiochromone**, by H. Simonis and A. Elias; and with **naphthodioxime**, and **naphthothioxime**, by B. Ghose and S. Smiles. G. Champetier represented the reaction of **phenyl magnesium bromide** on ferric chloride by the equations: (i)  $6\text{C}_6\text{H}_5\text{MgBr} + 2\text{FeCl}_3 \rightarrow 3(\text{C}_6\text{H}_5)_2 + 2\text{Fe} + 3\text{MgBr}_2 + 3\text{MgCl}_2$ ; (ii)  $2\text{C}_6\text{H}_5\text{MgBr} + 2\text{FeCl}_3 \rightarrow (\text{C}_6\text{H}_5)_2 + 2\text{FeCl}_2 + \text{MgBr}_2 + \text{MgCl}_2$ ; and (iii)  $2\text{C}_6\text{H}_5\text{MgBr} + \text{FeCl}_2 \rightarrow \text{Fe} + \text{MgBr}_2 + \text{MgCl}_2$ . E. Beckmann found that the salt is soluble in **benzil**. The complex with **urea** was studied by G. A. Barbieri; and with **tetra-phenylurea**, by R. H. Pickard and J. Kenyon. S. C. De and T. K. Chakravorty studied the action of ferric chloride and hydrogen dioxide on **thiosemicarbazones**.

A. Benrath found that ferric chloride dissolves in **formic acid**, and when the soln. is warmed, hydrogen chloride escapes, and on cooling, crystals of **ferric chloroformate**,  $\text{FeCl}(\text{H.COO})_2 \cdot 0.5\text{H}_2\text{O}$ , are deposited. A. Rosenheim and P. Müller studied this reaction; V. Macri, the decolorization of a soln. of ferric chloride by formic acid; A. Benrath, the decomposition of the soln. in sunlight with the evolution of carbon dioxide; and A. Quartaroli, the magnetic properties (*q.v.*) of the soln. J. Timmermans, and A. W. Davidson found that ferric chloride is soluble in **acetic acid**, and the soln. slowly deposits a reddish-brown precipitate. R. Weinland and co-workers studied the complex salts formed by the action of ferric chloride on acetic acid. A. Benrath observed that the soln. of ferric chloride in acetic acid is stable in light. A. Quartaroli studied the magnetic properties (*q.v.*) of the soln.; V. Macri, the action of acetic acid; and R. Weinland and A. Höhn, R. Weinland and H. Hachenburg, and R. Grünberg-Krasnowskaja, the complex chloroacetates. L. Kahlenberg and A. T. Lincoln observed that ferric chloride forms with **acetic anhydride** a soln. which is electrically a conductor. A. Benrath found that ferric chloride, or its hexahydrate, forms a dark brown soln. with **propionic acid**, and the soln. slowly deposits crystals of **ferrous chloropropionate**,  $\text{FeCl}(\text{C}_2\text{H}_5\text{COO})$ . R. Weinland and A. Höhn studied the complex salts with propionic acid. J. Timmermans observed that ferric chloride is insoluble in **stearic acid**. J. W. Döbereiner, J. M. Eder, and G. Lemoine showed that **oxalic acid** displaces most of the hydrochloric acid from ferric chloride, and that under the influence of light, the oxalic acid is oxidized to carbon dioxide. In darkness, the reaction begins at 50°, and increases in speed up to 100°. The reaction was studied by F. V. Jodin, A. Jodbauer, E. Baur, M. Roloff, J. Fiedler, M. Padoa, M. Padoa and N. Vita, A. J. Allmand and W. W. Webb, E. Menke, G. Kornfeld and E. Mencke, A. K. Sanyal and N. R. Dhar, A. Benrath and co-workers, E. Shpolsky, H. Kunz-Krause and P. Manicke, R. F. Weinland and F. W. Sierp, E. Marchand, A. J. Allmand and K. W. Young, and B. K. Mukerji and N. R. Dhar. Actinometers based on the reaction were devised by J. W. Draper, H. N. Draper, L. Warnerke, E. Marchand, G. Kornfeld and E. Mencke, A. Lipowitz, and T. Woods. J. C. Ghosh and R. M. Purkayastha, and R. M. Purkayastha studied the action of light on soln. of ferric chloride in **lactic, tartaric, and mandelic acids**; A. Benrath and K. Schaffganz, the photochemical reaction between tartaric acid and ferric chloride; S. Hakomori, the formation of complexes with tartaric acid; and J. C. Ghosh and B. N. Mitra, the extinction coeff. of soln. of ferric chloride in formic, acetic, propionic, oxalic, lactic, tartaric, mandelic, **malonic, succinic, glycollic, and citric acids**. C. V. Smythe found that a mixture of ferric chloride with lactic, glycollic, oxalic, tartaric, citric, or **malic acid**, is more acidic than is the case with the acid alone. This is explained by the formation of complexes and the hydroxylic ions. The reactions with citric and malic acids were studied by R. M. Purkayastha. The organic acid is oxidized by exposure to light. The results may be explained by supposing that there is an equilibrium in soln. between ferric chloride and acid as reactants and an intermediate complex formed by the loose combination of one mol. of each of the reactants, and by assuming a definite value of the molecular

extinction coeff., for each wave-length, for the intermediate complex so formed. V. Macri studied the action of tartaric acid. W. D. Treadwell and W. Fisch studied the complexes formed with **dicarboxylic acids**; and C. Morton, with **salicylic acid**. J. H. Walton and D. P. Graham studied the oxidation of the dicarboxylic acids with ferric chloride and hydrogen dioxide. The complex with **benzhydroxamic acid** was studied by R. Weinland and G. Baier; and with **cinnamic acid**, by A. Rosenheim and W. Levy.

P. C. Ray and P. C. Mukherjee obtained complex salts with **ethyl sulphide** and with **1:4-dithian**. L. I. Shaw found that ferric chloride is soluble in **dimethyl sulphate**. L. Kahlenberg and A. T. Lincoln, and A. T. Lincoln studied the electrical conductivity (*q.v.*) of soln. of ferric chloride in **amyl nitrite**; in **ethyl nitrate**—good conductor; in **ethyl chlorocarbonate**—good conductor; and **ethyl carbonate**—non-conductor; L. Kahlenberg, soln. in **methyl thiocyanate**, in **ethyl thiocyanate**, in **amyl thiocyanate**, and in **ethyl isothiocyanate**. L. Kahlenberg said that ferric chloride is soluble in **allyl isothiocyanate**. J. Rill, and A. Naumann and J. Rill observed that ferric chloride is soluble in **methyl acetate**, forming a yellow soln., which E. Busch said becomes deeper in colour and finally brown. A. Quartaroli studied the magnetic properties (*q.v.*). J. Allain le Canu, E. Alexander, A. Naumann and E. Alexander found that ferric chloride is soluble in **ethyl acetate**. The mol. refraction (*q.v.*) of the soln. was studied by J. H. Gladstone; the electrical conductivity (*q.v.*) by L. I. Shaw, and L. Kahlenberg and A. T. Lincoln; and the magnetic properties (*q.v.*) by A. Quartaroli. W. F. O. de Coninck observed that the yellow, dil. soln. is stable in light; and it is decolorized by filtration through animal charcoal. L. Kahlenberg and A. T. Lincoln, L. Kahlenberg, and E. Pietsch and co-workers studied the action of **sodium acetate** on ferric chloride in ethereal soln. W. D. Treadwell and W. Fisch studied the complexes formed with acetates. A. T. Lincoln observed the electrical conductivities of soln. of ferric chloride in **propyl acetate**—poor conductor; in **butyl acetate**—poor conductor; in **amyl butyrate** and **amyl valerianate**—poor conductors; and in **ethyl monochloroacetate**, **ethyl cyanoacetate**, **diethyl oxalate**, **ethyl acetoacetate**, and **ethyl benzoate**. L. Letellier studied the reaction with ethyl acetoacetate. The complex with **ethyl cinnamate** was studied by A. Rosenheim and W. Levy; and with **trimethyl thiophosphate**, by P. Pistschimuka. K. Charitschkoff said that **naphthenic acid** reduces ferric to ferrous chloride; and E. S. Hill studied iron as a catalyst in the oxidation of **dialuric acid**.

L. Kahlenberg and A. T. Lincoln found that ferric chloride dissolves in **nitrobenzene**, and the lowering of the f.p. indicates a decrease in the mol. wt. with increasing conc.; they also measured the electrical conductivity (*q.v.*) of the soln.; and L. Kahlenberg, the e.m.f. of cells with this soln. (*q.v.*). Similarly also with soln. of ferric chloride in **m-nitrotoluene**, and in **o-nitrotoluene**. F. L. Shinn found that a sat. soln. of ferric chloride in **ethylamine** has a sp. conductivity of  $13.5 \times 10^{-6}$  mho at 0°; and H. McKee Elsey said that a complex salt is formed. L. Kahlenberg, L. Kahlenberg and O. E. Ruhoff found that ferric chloride dissolves slowly in **amylamine**, and the soln. are electrically conducting (*q.v.*). J. Schröder, and A. Naumann and J. Schröder observed that the soln. of ferric chloride in **pyridine** is reddish-yellow, and probably contains a complex salt. A. Werner and W. Schmuylhoff studied the mol. raising of the b.p. The electrical conductivity—*vide supra*—was studied by L. Kahlenberg and A. T. Lincoln, and A. T. Lincoln; A. Quartaroli found that paramagnetic ferric chloride and diamagnetic pyridine give a magnetically inactive soln. with 14.160 grms.  $\text{FeCl}_3$  per litre. J. Schröder observed that the reddish-yellow soln. becomes darker with time; and when heated in a sealed tube, F. Hein and W. Retter observed a condensation of the pyridine to  $\alpha\alpha'$ -dipyridyl occurs. Water added to the soln. precipitates the iron as ferric hydroxide. The complex with pyridine was studied by G. Spacu, N. Costachescu and G. Spacu, R. F. Weinland and O. Schmid, and R. F. Weinland and A. Kissling; with  $\alpha\alpha'$ -**dipyridyl**, by F. Blau; with **antipyrine**, by R. F. Weinland and O. Schmid,

L. A. Welo, F. Hasse, Knoll and Co., A. Astruc and J. Bouisson, and M. C. Schuyten ; and with **pyramidon**, by R. F. Weinland and O. Schmid ; E. Beckmann observed that ferric chloride is soluble in boiling **quinoline**, and L. Kahlenberg and A. T. Lincoln added that the soln. is electrically conducting. The complex with quinoline was studied by R. Weinland and co-workers ; and W. Franke studied the system ferric iron and **quinol**. E. F. Wesp and W. R. Brode studied the spectra of compounds of ferric chloride and **phenol**. J. Timmermans observed that **dipropylamine** dissolves less than 0.5 per cent. of ferric chloride ; and, added O. Stephani, the solvent and solute react chemically ; he also found that **aniline** dissolves over 0.5 per cent. of ferric chloride, and L. I. Shaw, and L. Kahlenberg and A. T. Lincoln said that the soln. is a poor conductor of electricity. A. Forster and co-workers observed that a compound is formed with aniline and ferric chloride in ethereal soln. Y. Osaka and co-workers studied the system : ferric chloride, water, and aniline at 25°. The complex with aniline was studied by A. R. Leeds, and J. L. C. Schröder van der Kolk ; with *p*-**nitrosodi-*n*-butylaniline**, by J. Reilly, and J. Reilly and W. J. Hickinbottom. J. Timmermans said that **piperidine** dissolves over 0.5 per cent. of ferric chloride, but L. Kahlenberg and A. T. Lincoln said that the salt is insoluble in piperidine, and in **xylydine**—both meta, and asymmetric ; the soln. in **monomethylaniline**, **dimethylaniline**, *o*-**toluidine**, *m*-**toluidine**, and in **benzylamine** are poor conductors. W. H. Patterson studied the action of ferric chloride on *o*-, *m*-, and *p*-toluidine. E. Busch, A. Schier, and A. Naumann and A. Schier observed that the soln. of ferric chloride in **acetonitrile** is blood-red when conc., and yellowish-red when dil. ; the presence of dry hydrogen chloride makes the soln. pale yellow. The complex with **hexamethylenetetramine** was studied by L. Vanino and A. Schinner, and J. C. Duff and E. J. Bills observed that with boiling soln., ferric hydroxide is precipitated. Complex salts with **benzidine** were studied by G. Spacu, and A. Simon and T. Reetz ; with **tetramethyldiaminotriphenylamine**, by W. Madelung and co-workers ; with **ethyl carbylamine**, and **phenylcarbylamine**, by K. A. Hofmann and G. Bugge. J. Kämmerer, and A. Naumann observed that yellow soln. are formed by ferric chloride in **benzonitrile**, and L. Kahlenberg and A. T. Lincoln, and L. I. Shaw found that soln. are good electric conductors. G. Kornfeld found that ferric chloride dissolves in **formamide** like it does in water. He measured the mol. lowering of the f.p., and observed that the soln. may be kept unchanged at 0°, but not at room temp. T. Murayasu found that the electrical conductivity of ferric chloride soln. is increased by the addition of **glycocoll**. W. Eidmann found that ferric chloride is soluble in dry **methylal**, and E. Busch added that at 18°, the sat. soln. contains 20.28 grms. FeCl<sub>3</sub> in 100 grms. of soln. He measured the mol. raising of the b.p. The dark green soln. does not decompose in daylight ; and it becomes reddish-brown when treated with a small proportion of water ; the soln. absorbs hydrogen chloride and becomes intensely green. The solubility of ferric chloride in methylal saturated with water at 18° is 47.35 grms. FeCl<sub>3</sub> per 100 grms. of soln. J. Timmermans found that **sulphonal** dissolves over 0.5 per cent. of ferric chloride ; T. Chakrabarti and S. De studied the action of ferric chloride on **thiocarbamides** ; G. Fuseya and K. Murata, and T. Murayasu studied the complexes formed by iron salts with **glycine** ; R. M. Purkayastha, with **sugars** ; and W. Franke, with **hydroquinone**. W. D. Bancroft and co-workers studied the photochemical reduction of soln. of ferric chloride in the presence of **organic dyes**.

G. Klose observed that 100 grms. of **lanolin**, of m.p. 46°, dissolve 4.17 grms. of FeCl<sub>3</sub> at 45°. M. Scholtz observed the formation of complexes with many **alkaloids**. The action of ferric chloride on **albumin** was studied by H. Bechhold, G. Buchner, A. Brossa and H. Freundlich, H. J. M. Creighton, G. Grasser, E. Heymann and F. Oppenheimer, I. G. Oberhard, W. Pauli and L. Flecker, H. Schorn, and A. W. Thomas ; on **casein**, by H. Palme ; on **hæmoglobin**, by H. Freundlich and G. Lindau ; on **gelatin**, by H. J. M. Creighton, R. E. Liesegang, L. Cramer, and M. Schneider ; on **soap** soln., by P. Verbeck ; W. Thomson and F. Lewis, **india-rubber** ; T. Katsurai, **milk** ; and on **wool**, by N. Schiloff. The retarding influence

of gelatin on the hydrolysis of the aq. soln. of ferric chloride was observed by C. L. Wagner, A. Tian, N. R. Dhar and D. N. Chakravarti, and R. E. Liesegang; and on **cellulose**, by W. Kopaczewsky and M. Rosnowsky. The action of ferric chloride in the tanning of **animal skins** was described by J. Jettmar; in the classification of **sewage**, by L. H. Enslow, F. Fischer, and A. Gärtner; and in the precipitation of **bacteria**, by O. Schwarz.

H. Moissan said that **boron** reduces ferric chloride in aq. soln. to ferrous chloride; but P. Lebeau observed no reduction when finely-powdered **silicon** is boiled for a long time with a 10 per cent. soln.—nor is the silicon perceptibly attacked. H. Moissan and S. Smiles found that a soln. of ferric chloride is readily attacked by **silicoethane**. O. Hönigschmid and co-workers observed that at a high temp. **quartz** is attacked by anhydrous ferric chloride. A. Tian, and N. R. Dhar and D. N. Chakravarti discussed the action of silica gel on the soln. J. R. Glauber, G. J. Mulder, and E. Jordis and W. Hennis observed the formation of an "iron tree" when a crystal of the hexahydrate is added to a conc. soln. of **sodium silicate**; and R. C. Ray and P. B. Ganguly, the formation of silica gels by the action of ferric chloride on alkali silicate soln. M. Schneider found that when ferric chloride soln. are boiled in **glass** vessels, a product of the hydrolysis adheres to the walls of the vessel; no such adsorption occurs if the soln. is acidified. P. Rohland, and J. J. Shukoff and M. N. Sokolova noted the adsorption of ferric chloride from its aq. soln. by **clays**. L. Wunder observed that **ultramarine** is decomposed in the cold by a soln. of ferric chloride, and hydrogen sulphide is evolved. O. C. Magistad studied the exchange of bases in **zeolites**.

According to H. Plauson and G. Tischtschenko, anhydrous ferric chloride is reduced to ferrous chloride when it is fused with **sodium**. P. Nicolardot, and W. Biltz and W. Holverschheit found that sodium dissolves in a conc. hydrochloric acid soln. of ferric chloride, hydrogen is evolved, but little or no reduction of the ferric chloride occurs. P. Jannasch and T. W. Richards observed that very little reduction of the soln. occurs with sodium amalgam, and D. Tommasi found that some ferric hydroxide is precipitated by the action of the amalgam. J. N. von Fuchs, L. Storch, E. Beutel and A. Kutzlignig, A. Pickles, T. W. Hogg, F. Fischer, D. Miklosich, and W. C. Birch observed that ferric chloride is reduced to ferrous chloride by finely-divided **copper**. The dissolution of copper by soln. of ferric chloride was observed by W. Weissenberger, and M. Mayer. E. Bekier and S. Trzeciak observed that in the presence of an excess of ammonium chloride, the action of copper on a soln. of ferric chloride can be symbolized:  $\text{Cu} + 2\text{FeCl}_3 \rightarrow \text{CuCl}_2 + 2\text{FeCl}_2$ , followed by  $\text{Cu} + \text{CuCl}_2 \rightarrow 2\text{CuCl}$ . The velocity constant of the reaction  $k = \{\log_e(a - \frac{1}{2}x_1) - \log_e(a - \frac{1}{2}x_2)\}v/S(t_2 - t_1)$ , where  $a$  denotes the initial conc. of ferric and cupric chlorides;  $\frac{1}{2}x_1$ , and  $\frac{1}{2}x_2$ , the conc. of the ferric and cupric chlorides at the times  $t_1$  and  $t_2$  respectively; and  $S$ , the surface area of the plate. With the rate of stirring 1500 per min.,  $k$  is 0.1508 at 15°, and 0.2044 at 25°, so that the temp. coeff. is 1.35 between 15° and 25°; the value of  $k$  is independent of the composition of the soln. starting with ferric chloride and ending with cupric chloride as the sole active constituents; and it increases with the rate of stirring. The value of  $k$  increases up to a limiting value as the conc. of the ammonium chloride increases, but beyond that stage it is independent of the conc. of the ammonium chloride. P. Schulz observed that in acetone soln., copper slowly reduces ferric chloride to ferrous chloride; and J. Schröder obtained a similar result in pyridine soln. G. Wetzlar found that powdered **silver** reduces an aq. soln. of ferric to ferrous chloride. The reaction was studied by N. A. Tananaeff, E. Beutel and A. Kutzlignig, and S. A. Voznesensky and V. Skvorzoff. P. Schulz observed no reduction in acetone soln., but J. Schröder observed that the reduction occurs in pyridine soln. C. St. Pierre, and J. Napier found that a dil., feebly acidic soln. of ferric chloride dissolves traces of **gold**, but J. Nickles said that no dissolution occurs with cold or hot soln. P. Nicolardot, and D. J. Carnegie said that the soln. of ferric chloride is not reduced by gold, but G. Wetzlar said that some ferric chloride

is reduced by the gold. H. Schild said that  $0.1N\text{-FeCl}_3$  at ordinary temp. slowly attacks gold forming aurous and ferrous chlorides. P. C. McIlhiney pointed out that a dil. soln. of ferric chloride in conc. hydrochloric acid does not attack gold if heated in a sealed tube provided air be excluded, but in the presence of air, the ferric chloride acts as a carrier of chlorine to the gold. H. N. Stokes used a 20 per cent. soln. of ferric chloride in half its vol. of 20 per cent. hydrochloric acid, free from nitric acid, and observed that at  $200^\circ$  there is a slow reaction  $\text{Au} + 3\text{FeCl}_3 \rightleftharpoons \text{AuCl}_3 + 3\text{FeCl}_2$ , which is reversed in the cold.

L. Hackspill found that at a dull red-heat, **calcium** reduces anhydrous ferric chloride:  $2\text{FeCl}_3 + 3\text{Ca} = 3\text{CaCl}_2 + 2\text{Fe} + 317.4 \text{ Cals.}$  W. Biltz and W. Holverscheid observed no reduction of ferric chloride dissolved in conc. hydrochloric acid, although much hydrogen is developed. H. Plauson and G. Tischtschenko observed that when ferric chloride is melted with **magnesium** in an atmosphere of hydrogen, ferrous chloride is formed; and K. Seubert and A. Schmidt found that at a dull redness, the mixture becomes very hot, and the reaction proceeds violently forming magnesium and ferrous chlorides, and iron. J. Michajlenko and P. Muschinsky found that when a mixture of magnesium and hexahydrated ferric chloride is triturated at room temp., some hydrogen is evolved. S. Kern represented the reaction in aq. soln. by  $2\text{FeCl}_3 + 3\text{Mg} + 6\text{H}_2\text{O} = 2\text{Fe}(\text{OH})_3 + 3\text{MgCl}_2 + 3\text{H}_2\text{O}$ , when the soln. is free from dissolved air, and no reduction was observed by D. Tommasi. W. Biltz and W. Holverscheid observed no reduction in conc. hydrochloric acid soln. although hydrogen is copiously evolved; P. Jannasch and T. W. Richards observed a very incomplete reduction; and D. J. Carnegie, and H. N. Warren said that reduction is complete. K. Seubert and A. Schmidt observed that in warm, neutral soln., some ferrous hydroxide is precipitated; and D. Vitali obtained hydrogen, hydrated ferrous oxide, ferrous chloride, and iron as products of the reaction. K. Seubert and A. Schmidt, and A. Hönig also observed the precipitation of iron in acidic soln. P. Schulz found that magnesium slowly reduces ferric to ferrous chloride in acetone soln., and J. Schröder obtained similar results in pyridine soln. K. Schwenzer studied the reduction in ethereal soln. M. A. Parker and H. P. Armes observed that the reduction of ferric chloride in acidic soln. by magnesium is not influenced by a magnetic field. G. Wetzlar, and J. Napier found that **zinc** reduces ferric to ferrous chloride in aq. soln. D. J. Carnegie—*vide supra*, nascent hydrogen—supposed that the reduction by zinc dust is direct, and not *viâ* nascent hydrogen. If acid be not present, hydrated ferrous and ferric oxides are formed. According to E. Beutel and A. Kutzlknigg, a soln. of ferric chloride containing less than 100 grms. per litre has no effect on a bright surface of zinc, but more conc. soln. give a deposit containing iron. The rate of deposition increases with the conc. of the soln. until an optimum conc. of 500 grms. per litre is attained. A matt surface of zinc, obtained by a sand-blast, is slowly darkened by soln. with 50 grms. of  $\text{FeCl}_3$  per litre. The spongy, non-adherent, grey layer has a metallic lustre, and contains irregular, microscopic granules of zinc and iron. The treatment of the deposit with distilled water gives no rust, but minute filaments of zinc hydroxide are formed. If sheet zinc be exposed for a long time to the action of soln. containing 500 to 1000 grms. of ferric chloride per litre, the primary deposit of iron is converted into compact, dark brown, hydrated ferric oxide. The hydrolysis of ferric chloride soln. furnishes hydrochloric acid which attacks the zinc, depositing a quantity of ferric hydroxide corresponding with the acid used in the production of zinc chloride. Some ferrous chloride is formed. The primary iron deposit formed in conc. ferric chloride soln. appears to undergo, more or less rapidly according to the degree of concentration, a change giving a brilliant, lustrous, but extremely brittle metallic layer, which breaks up spontaneously on reaching a certain thickness; this is found to be about  $9 \times 10^{-3}$  mm. The deposit contains zinc, and its composition varies with the concentration of the ferric chloride soln. Grey deposits are also obtained with alcoholic ferric chloride soln., and with dil. or conc. aq. ferrous sulphate. A coherent, tenacious, dove-grey deposit is similarly

produced in the presence of fluoride ions, whilst addition of a colloid (glue) yields a soln. which appears to contain iron as a dispersed phase, since after removal of a black deposit it possesses a dull grey colour. P. Schulz observed that zinc reduces ferric to ferrous chloride in acetone soln. The reduction of ferric to ferrous salts by zinc is utilized in analytical chemistry. D. L. Randall, L. Moyaux, and A. L. Beebe recommended amalgamated zinc, or amalgamated zinc in contact with platinum; G. T. Morgan, and J. H. Gladstone, a copper-zinc couple; and A. Gemmell, a zinc-magnesium or zinc-aluminium alloy. S. S. Bhatnagar and co-workers said that the reduction of ferric salts by zinc is reduced by a magnetic field; but M. Loeb, and F. A. Wolff obtained negative results in their examination of the influence of a magnetic field on the oxidation and reduction of iron salts. E. Beutel and A. Kutzlugg studied the film of iron sometimes precipitated on zinc in soln. of over 100 grms.  $\text{FeCl}_3$  per litre. J. Napier found that **cadmium** reduces an aq. soln. of ferric to ferrous chloride; and W. Heller studied the velocity of dissolution of cadmium in an aq. soln. of ferric chloride. P. Schulz observed that the reduction occurs slowly in acetone soln.; and J. Schröder, in pyridine soln. L. Wolf, D. Tommasi, D. J. Carnegie, and P. Nicolardot observed that a dil. acidified soln. of ferric chloride is reduced to ferrous chloride by **mercury**; and L. Meyer, and D. Borar said that in aq. soln. some mercurous chloride is formed. L. Q. McCay and W. T. Anderson, and P. Süss found that with vigorous shaking, the reduction  $\text{FeCl}_3 + \text{Hg} = \text{FeCl}_2 + \text{HgCl}$  is complete in a few minutes. H. Schild added that at ordinary temp., 0.1N- $\text{FeCl}_3$  forms mercurous chloride, and at higher temp., mercuric chloride is formed. S. Popoff and co-workers found for the reaction  $2\text{Fe}^{+++} + 2\text{Hg} \rightleftharpoons 2\text{Fe}^{++} + \text{Hg}_2^{++}$  the equilibrium constant 0.0180. Amalgamated zinc is also used for reducing ferric chloride.

E. Berger observed that a vigorous reduction occurs once the temp. of a mixture of powdered **aluminium** and anhydrous ferric chloride has been raised high enough to start the reaction. D. J. Carnegie, C. L. Schumann, F. J. R. Carulla, and W. H. Seamon reduced aq. soln. of ferric chloride to ferrous chloride. J. M. Weeren observed that the reaction proceeds more rapidly in vacuo than at ordinary press. H. Schild said that with neutral 0.1N- $\text{FeCl}_3$ , the soln. becomes dark red, and later a basic chloride is deposited, and ferrous chloride and hydrogen are produced. A. Hoenig added that the reduction is complete, and that, as in the case of magnesium and zinc, some iron is deposited. The solubility of aluminium in soln. of ferric chloride was studied by W. Heller. P. Schulz observed a slow reduction of ferric chloride in acetone soln.; and J. Schröder, in pyridine soln. F. Burkert, and H. H. Potter and W. Sucksmith used a soln. of ferric chloride for producing a film on aluminium, and also for etching the metal. M. A. Parker and H. P. Armes said that the reduction of ferric chloride in hydrochloric acid soln. by aluminium is influenced by a magnet; and S. S. Bhatnagar and co-workers said that, unlike the case with zinc, the reduction by aluminium is accelerated in a magnetic field. M. Loeb, and F. A. Wolff obtained negative results in similar cases of reduction.

G. Wetzlar, and J. Napier observed that a soln. of ferric chloride is reduced by **tin** to ferrous chloride at ordinary temp. H. Schild said that the conditions determine whether stannic or stannous chloride is formed. W. Heller studied the rate of dissolution of tin in an aq. soln. of ferric chloride. R. Kremann and F. Noss discussed the reaction  $\text{Sn} + 2\text{FeCl}_3 = \text{SnCl}_2 + 2\text{FeCl}_2$ . W. Biltz and W. Holverscheid found that with a 6 per cent. soln. of  $\text{FeCl}_3$ , and 25 per cent. of  $\text{HCl}$ , no hydrogen is developed, and the reaction proceeds  $\text{Sn} + 4\text{FeCl}_3 = \text{SnCl}_4 + 4\text{FeCl}_2$ , with higher concentrations of acid, hydrogen is developed, and with higher concentrations of ferric chloride, the speed of the reaction is reduced. P. Schulz observed that tin slowly reduces a soln. of ferric chloride in acetone; and J. Schröder, a soln. in pyridine. I. A. Lösner said that a sat. aq. soln. of ferric chloride dissolves tin, and W. Heller said that the rate of soln. is proportional to the temp., and to the rate of stirring, but the temp. coeff. of the reaction is independent of the rate of stirring. The de-tinning of iron by soln. of ferric chloride was discussed by B. Schultze, and



R. Garcia. G. Wetzlar, J. Napier, H. Schild, and G. J. Hough found that **lead** reduces a soln. of ferric to ferrous chloride. J. Napier added that the action in a neutral soln. of ferric chloride is soon hindered by the formation of a protective crust of lead chloride; a boiling soln. acts more vigorously forming a deposit of hydrated ferric oxide. F. Stolba showed that the reduction of the ferric chloride proceeds rapidly with a hydrochloric acid soln. of ferric chloride containing some sodium chloride. P. Schulz said that lead does not act on an acetone soln. of ferric chloride.

E. F. Smith and H. C. Burr observed that **molybdenum** rapidly reduces a soln. of ferric to ferrous chloride, and molybdenum hexachloride is formed,  $6\text{FeCl}_3 + \text{Mo} = 6\text{FeCl}_2 + \text{MoCl}_6$ . C. H. Ehrenfeld said that the reaction in very dil., feebly acidified soln. of ferric chloride is complete. O. Jochem noticed that colloidal molybdenum reduces ferric chloride soln. C. H. Ehrenfeld found that **tungsten** attacks the soln. of ferric chloride with difficulty. H. Schild observed that **manganese** reduces 0.1N- $\text{FeCl}_3$  at ordinary temp. forming ferrous and manganous chlorides.

G. Wetzlar, and J. Napier observed that **iron** reduces an aq. soln. of ferric chloride; and J. Thomsen gave for the reaction  $2\text{FeCl}_3 + \text{Fe} = 3\text{FeCl}_2 + 44.41$  Cals. Observations were also made by T. Andrews, and M. Berthelot; and M. Troilius found that with commercial iron, the iron oxide, sulphide, and phosphide, silica, and carbon remain as a residue, whilst the iron dissolves in the conc. soln. of ferric chloride. W. Spring thought that although ferric chloride soln. readily attack ordinary iron, it will probably not dissolve purified iron. The speed of the reaction increases with increasing dilution of the soln., and with less than 80 grms. of ferric chloride to 100 of water, there are two different reactions involved: (i) the direct dissolution of iron, and (ii) the action of hydrochloric acid, produced by hydrolysis, on the iron—the latter reaction is accompanied by the evolution of hydrogen. With 0.1N- $\text{FeCl}_3$ , H. Schild obtained a deposit of a basic chloride. The reaction was also studied by I. A. Lösner, W. Jufereff, D. J. Carnegie, W. H. Carothers and R. Adams, and R. G. van Name and D. U. Hill. D. A. McInnes and A. W. Contieri observed that by decreasing the external press., there is a slowing down of the reaction attended by the liberation of hydrogen, and an increase in the yield of ferrous chloride; in a feebly acidic soln., reducing the press. from 760 to 80 mm. increased the yield of ferrous chloride five times. A. F. Gehlen observed that iron reduces ferric to ferrous chloride in ethereal soln. M. A. Parker and H. P. Armes showed that the reduction of an hydrochloric acid soln. of ferric chloride, by metallic iron or aluminium, and the reduction of permanganate in acid soln. by metallic iron, are hastened in the magnetic field, there being a definite relationship between the extent of reduction and the strength of the field. The phenomena observed during the reduction of ferric chloride in hydrochloric acid soln. by magnesium are attributed to the formation of a magnetic deposit on the metal. The effect of stirring the soln. during reduction diminishes the difference in the extent of reduction in a given time in and out of the field. S. S. Bhatnagar and co-workers found that the reduction of ferric chloride soln. by iron, and aluminium is accelerated by a magnetic field. M. Loeb, and F. A. Wolff obtained negative results in examining the effect of a magnetic field on the reduction and oxidation of iron salts. J. Napier found that a neutral, aq. soln. of ferric chloride is quantitatively reduced by **cobalt** or **nickel** to ferrous chloride; and similar results were obtained by H. Schild, H. H. Potter and W. Sucksmith, H. N. Huntzicker and L. Kahlenberg, and H. S. Rawdon and M. G. Lorentz. P. Schulz found that cobalt and nickel do not act on ferric chloride in acetone soln.

C. St. Pierre, and R. Böttger found that a dil., feebly acid soln. of ferric chloride is reduced to ferrous chloride by boiling with **palladium** rather more quickly than is the case with platinum:  $\text{Pd} + 2\text{FeCl}_3 = \text{PdCl}_2 + 2\text{FeCl}_2$ . The transformation is quantitative; and A. C. Chapman observed that if the palladium be charged with hydrogen, the reduction occurs without the palladium dissolving—*vide supra*,

hydrogen. According to A. Béchamp and C. St. Pierre, C. St. Pierre, D. Tommasi, H. Schild, and P. Nicolardot, **platinum** is dissolved by a soln. of ferric chloride:  $\text{Pt} + 2\text{FeCl}_3 = \text{PtCl}_4 + \text{FeCl}_2$ . Freshly precipitated platinum, indeed, is completely dissolved in 10 mins. by the boiling soln., platinum sponge which has been heated to redness dissolves gradually in a hydrochloric acid soln. of ferric chloride. J. Napier, D. J. Carnegie, and C. Marie reported that ferric chloride is not reduced by platinum—*vide supra*, hydrogen. E. Baur noted that 5 to 10 c. mm. of gas, probably oxygen, is developed when platinum gauze is dipped in 10 c.c. of  $M\text{-FeCl}_3$ . B. H. Buxton and O. Teague, and H. D. Murray studied the coagulation of colloidal soln. of platinum by ferric chloride. C. R. A. Wright and C. Thompson found that a cell with platinum plates respectively in an alkaline soln. and in an acid soln. of ferric chloride furnishes a current, and oxygen is given off from the alkaline soln., and hydrogen from the acid soln.

For the action of **alkali hydroxides**, *vide supra*, the analytical reactions of iron. L. L. de Koninck found that **cuprous oxide** reacts with an acidified soln. of ferric chloride:  $\text{Cu}_2\text{O} + 2\text{FeCl}_3 + 2\text{HCl} = 2\text{CuCl}_2 + 2\text{FeCl}_2 + \text{H}_2\text{O}$ ; and R. K. Meade obtained an analogous result with **cuprous hydroxide**. O. Ruff and B. Hirsch, K. List, and E. Kopp observed that **cupric oxide** rapidly decomposes a neutral, aq. soln. of ferric chloride forming a brown, cupriferous precipitate.

E. Kothny found that anhydrous ferric chloride reacts rapidly with cupric oxide,  $3\text{CuO} + 2\text{FeCl}_3 = 3\text{CuCl}_2 + \text{Fe}_2\text{O}_3$ ; and at  $600^\circ$ , the reaction is completed in 15 mins. A. Béchamp observed that with **cupric hydroxide** dissolved in the soln. of ferric chloride, hydrated ferric oxide is precipitated, and subsequently dissolved. A soln. with a mol of ferric chloride takes up 1.25 mol of cupric oxide. The addition of cupric chloride to the sat. soln. precipitates the iron. N. Pappada also noted the peptization of cupric hydroxide by a soln. of ferric chloride. P. Nicolardot found that **silver oxide** precipitates hydrated ferric oxide from a dil. soln. of ferric chloride. A. Daubrée found that the vapour of ferric chloride passed over **calcium oxide** yields crystals of hæmatite; and J. M. van Bemmelen and E. A. Klobbie said that the product is calcium ferrite, not hæmatite. A. Béchamp observed that **zinc oxide** behaved very much like cupric hydroxide. J. Volhard noted that zinc oxide completely precipitates hydrated ferric oxide mixed with some zinc oxide from a soln. of ferric chloride at ordinary temp. P. Nicolardot found that a soln. of ferric chloride dissolved a little over 1 per cent. of zinc oxide, and the soln. gave a yellow precipitate when warmed. O. Ruff and B. Hirsch, and N. Pappada noted the peptization of **zinc hydroxide** by a soln. of ferric chloride; and similarly also with **cadmium hydroxide**. N. G. Chatterji and N. R. Dhar found that an alkaline soln. of **alkali zincate** precipitates from ferric chloride hydrated ferric oxide contaminated with zinc hydroxide. H. Rose observed that **mercuric oxide** in excess precipitates all the iron as hydrated ferric oxide from a soln. of ferric chloride, and mercuric oxychloride is formed at the same time; J. Volhard also found that the reaction is quantitative at ordinary temp., and utilized it in the separation of iron from manganese; and the process was studied by P. Nicolardot, C. Meineke, E. F. Smith and P. Heyl, B. Finzi, O. Ruff and B. Hirsch, and C. Zimmermann. A. Mailhe added that the precipitate is ferric oxychloride, not hydroxide. N. Pappada studied the peptization of **mercuric hydroxide** by soln. of ferric chloride.

A. Béchamp found that neutral, aq. soln. of ferric chloride slowly dissolve freshly precipitated **aluminium hydroxide**; hydrated ferric oxide is precipitated, and the soln. is gradually decolorized. The reaction was studied by E. A. Schenider, and N. Pappada. The so-called *ferric-alumina* used as a coagulant in water-softening is essentially a colloidal soln. of alumina peptized by ferric chloride. It was discussed by W. D. Hatfield, A. R. Moberg, A. R. Moberg and E. M. Partridge, L. B. Miller, E. J. Theriault and W. M. Clark. N. G. Chatterji and N. R. Dhar observed that an alkali soln. of **alkali aluminate** precipitates hydrated ferric oxide mixed with hydrated alumina from a soln. of ferric chloride.

P. Nicolardot observed that **lead oxide** precipitates hydrated ferric oxide. A. Béchamp said that **chromic hydroxide** does not dissolve in a neutral soln. of ferric chloride, although a dil. soln. may be coloured olive-green, or brownish-green; but N. Pappada found that chromic hydroxide is dissolved by conc. soln. of ferric chloride. A. Geuther observed that when a mixture of anhydrous ferric chloride and **chromium trioxide** is heated, chromyl chloride is formed:  $2\text{FeCl}_3 + 3\text{CrO}_3 = \text{Fe}_2\text{O}_3 + 3\text{CrO}_2\text{Cl}_2$ ; and E. Comanducci observed that chromyl chloride is obtained by heating a mixture of **potassium dichromate**, ferric chloride, and conc. sulphuric acid. N. G. Chatterji and N. R. Dhar observed that with an alkaline soln. of **alkali chromite**, hydrated ferric oxide mixed with hydrated chromic oxide is precipitated. A. Geuther found that the reaction of **molybdenum trioxide** resembles that with chromium trioxide; and likewise also with **tungsten trioxide**. O. Ruff and B. Hirsch noted a reaction with **manganous hydroxide**; and W. Spring and G. de Boeck found that hydrated manganic oxide dissolves in aq. soln. of ferric chloride. The action of **ferric oxide and hydroxide** on soln. of ferric chloride is discussed in connection with the hydrosol, and hydrogel of ferric oxide. M. Kuhara found that when precipitated ferric hydroxide is boiled for a long time in 20 per cent. soln. of ferric chloride, hæmatite is formed. C. A. O. Rosell observed that ferric chloride is completely decomposed by **barium ferrate**, giving off chlorine, and oxygen, and forming ferric hydroxide and barium chloride. O. Ruff and B. Hirsch, and N. Pappada found that **cobalt hydroxide**, like ferric hydroxide, is peptized by a soln. of ferric chloride; and similarly with a soln. of **nickel hydroxide**. E. M. Walton observed that when the hexahydrate is triturated with **hexahydrated calcium chloride** liquefaction occurs. J. Schröder found that in pyridine soln. ferric chloride is completely reduced to ferrous chloride by **cuprous chloride**. R. Rosendahl studied the reaction. G. Herrmann, and S. G. Rawson found that cuprous chloride readily dissolves in a feebly acidified soln. of ferric chloride—*vide infra*; and C. Winther observed that the reduction  $\text{CuCl} + \text{FeCl}_3 = \text{FeCl}_2 + \text{CuCl}_2$  is quantitative; he also found that **mercurous chloride** dissolves in a warm soln. of ferric chloride forming ferrous and mercuric chlorides. The reaction is complete but slow at room temp., and in ultra-violet light, the reaction is reversible. The reaction was found by J. Woost to be accelerated by hydrochloric acid. G. Carobbi found that **molybdenum trichloride** reduces ferric to ferrous salts; and W. Wardlaw and R. L. Wormell obtained a similar result with **molybdenum oxychloride**,  $\text{MoOCl}$ . E. Beckmann said that ferric chloride is insoluble in **chromyl chloride**; and F. E. Brown and J. E. Snyder, insoluble in **vanadium oxytrichloride**. Ferric chloride in aq. soln. is reduced by **stannous chloride**:  $2\text{FeCl}_3 + \text{SnCl}_2 = 2\text{FeCl}_2 + \text{SnCl}_4$ . L. Kahlenberg said that the reaction is bimolecular in acidic soln., and A. A. Noyes found it to be trimolecular. The reaction  $\text{Sn}^{++} + 2\text{Fe}^{+++}$  was studied by F. G. Soper, W. C. Bray and M. H. Gorin, L. V. Pisarhevsky, and M. A. Rozenberg; and W. F. Timoféeff and co-workers investigated the accelerating action of neutral salts on the reduction of ferric chloride by stannous chloride. W. Schluttig titrated soln. of stannous chloride with ferric chloride, using indigo-carmin as internal indicator. E. M. Walton found that when the hydrate  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  is triturated with the hexahydrate liquefaction occurs. The action of stannous chloride on ferric chloride in acetone soln. was found by P. Schulz to be similar to that in aq. soln.; likewise by A. Schier, in acetonitrile soln.; by E. Busch, in methylal soln.; and by J. Schröder, in pyridine soln., forming a complex salt. L. F. Nilson observed that **hydrochloroplatinous acid** reduces ferric to ferrous chloride; and **hydrochloroplatinic acid** forms a chloroplatinate. P. Schulz observed a dirty white precipitate of silver chloride is produced when **silver nitrate** is added to an acetone soln. of ferric chloride; and E. Busch, a white precipitate in soln. of ferric chloride in methylal. E. M. Walton found that when the hexahydrate, or the hemipentahydrate is triturated with **enneahydrated ferric nitrate**, liquefaction occurs.

Aq. soln. of ferric chloride dissolve sulphides of the heavy metals when assisted

by heat. The action of **alkali sulphides** has been discussed previously—*vide supra*, the analytical reactions of iron. E. Kothny found that the anhydrous chloride at  $230^{\circ}$  in an indifferent gas reacts completely with **cuprous sulphide** in accord with  $4\text{FeCl}_3 + \text{Cu}_2\text{S} = 4\text{FeCl}_2 + 2\text{CuCl}_2 + \text{S}$ . J. B. Cammerer found cuprous sulphide is attacked at ordinary temp. by an aq. soln. of ferric chloride, and a little gas is given off by warm soln.—either at  $100^{\circ}$ , or in a sealed tube at  $120^{\circ}$ —the reaction occurs in two stages:  $\text{Cu}_2\text{S} + 2\text{FeCl}_3 = \text{CuCl}_2 + 2\text{FeCl}_2 + \text{CuS}$ , and  $\text{CuS} + 2\text{FeCl}_3 = \text{CuCl}_2 + 2\text{FeCl}_2 + \text{S}$ . J. B. Cammerer said that no cuprous chloride is formed, but L. Gabba represented the reaction:  $2\text{FeCl}_3 + \text{Cu}_2\text{S} = 2\text{FeCl}_2 + 2\text{CuCl} + \text{S}$ . The reaction was studied by E. F. Anthon, E. Burschell, and J. Hanus. J. B. Cammerer represented the reaction of a 3 per cent. soln. of ferric chloride on **cupric sulphide** at ordinary temp.,  $\text{CuS} + 2\text{FeCl}_3 = \text{CuCl}_2 + 2\text{FeCl}_2 + \text{S}$ ; with a boiling soln., some hydrogen sulphide and sulphur dioxide are formed. Similar results were obtained in a sealed tube at  $120^{\circ}$ . The reaction was studied by E. F. Anthon, E. Burschell, and J. Hanus. The utilization of the reactions in the extraction of copper from roasted sulphide ores was discussed by O. Chalandre, E. Cumenge and R. Wimmer, F. N. Flynn and R. H. Hatchett, E. Kopp, and G. P. Schweder; J. B. Cammerer represented the action of a 3 per cent. soln. of ferric chloride on **silver sulphide** by the equation:  $\text{Ag}_2\text{S} + 2\text{FeCl}_3 = 2\text{AgCl} + 2\text{FeCl}_2 + \text{S}$ . E. F. Anthon also studied the reaction of the soln. on silver sulphide, and on **cadmium sulphide**. F. Field found that neutral or acidic soln. of ferric chloride when boiled for a long time with **mercuric sulphide** form mercuric and ferrous chlorides, and sulphur, and, added J. B. Cammerer, with the intermediate formation of  $2\text{HgS} \cdot \text{HgCl}_2$ . J. B. Cammerer represented the action of a boiling, neutral soln. of ferric chloride on **stannous sulphide** by the equation:  $\text{SnS} + 4\text{FeCl}_3 = \text{SnCl}_4 + 4\text{FeCl}_2 + \text{S}$ ; and on **stannic sulphide**:  $\text{SnS}_2 + 4\text{FeCl}_3 = \text{SnCl}_4 + 4\text{FeCl}_2 + 2\text{S}$ . Traces of sulphuric acid are also formed; and some stannic hydroxide appears as a result of the hydrolysis of the stannic chloride. E. F. Anthon observed that precipitated **lead sulphide** reacts with a boiling soln. of ferric chloride. The reaction was studied by J. B. Cammerer, D. J. Carnegie, A. Levallois, and T. Rieckher; and L. Gabba represented the reaction by the equation:  $2\text{FeCl}_3 + \text{PbS} = 2\text{FeCl}_2 + \text{PbCl}_2 + \text{S}$ . E. F. Anthon studied the action of a soln. of ferric chloride on **manganese sulphide**; and J. B. Cammerer represented the action of a 3 per cent. soln. by the equation:  $\text{MnS} + 2\text{FeCl}_3 = \text{MnCl}_2 + 2\text{FeCl}_2 + \text{S}$ ; and with **ferrous sulphide**:  $\text{FeS} + 2\text{FeCl}_3 = 3\text{FeCl}_2 + \text{S}$ . If the ferrous sulphide has been obtained by a high temp. process, the rate of dissolution is slow; and M. Troilius added that when a cold, neutral, conc. soln. of ferric chloride is used as an etching liquid for iron or steel, the particles of included ferrous sulphide are not attacked. J. B. Cammerer represented the action of a boiling, 3 per cent. soln. of ferric chloride on **iron disulphide**, or **pyrite**, by the equation:  $\text{FeS}_2 + 2\text{FeCl}_3 = 3\text{FeCl}_2 + 2\text{S}$ ; **chalcopyrite** is also partially decomposed. H. N. Stokes, and W. Wardlaw and F. H. Clews found that hot soln. of ferric chloride are reduced by pyrite or **marcasite**, and some sulphuric acid is formed. L. L. de Koninck represented the reaction with finely-powdered pyrite, in a sealed tube, at  $170^{\circ}$  to  $200^{\circ}$ , by the equation:  $\text{FeS}_2 + 14\text{FeCl}_3 + 8\text{H}_2\text{O} = 15\text{FeCl}_2 + 2\text{H}_2\text{SO}_4 + 12\text{HCl}$ . S. I. Levy and G. W. Gray represented the reaction with anhydrous ferric chloride and pyrite at  $500^{\circ}$  to  $1000^{\circ}$  by the equation:  $8\text{FeCl}_3 + 4\text{FeS}_2 = 12\text{FeCl}_2 + 8\text{S}$ —*vide pyrite and pyrrhotite*. E. F. Anthon, and J. B. Cammerer studied the action of the soln. of ferric chloride on **cobalt sulphide**:  $\text{CoS} + 2\text{FeCl}_3 = \text{CoCl}_2 + 2\text{FeCl}_2 + \text{S}$ ; and similar results were obtained with **nickel sulphide**.

F. L. Browne, and F. L. Browne and J. H. Mathews discussed the thermal value of the reaction between **sodium sulphate** and ferric chloride. P. Nicolardot observed that the addition of **alkali sulphate** to a dil. neutral, aq. soln. of ferric chloride results in the precipitation of a basic sulphate, but the reaction is complete only when the acidity of the soln. is very small. A boiling soln. of a gram of iron as  $\text{FeCl}_3$  per litre is completely precipitated by a gram of **ammonium sulphate**.

J. W. Retgers found that a mixed soln. of ferric chloride and ammonium-sulphate deposits colourless ammonium sulphate on evaporation. G. Lunge studied the solubility of **calcium sulphate** in soln. of ferric chloride. According to Z. Karaoglanoff, **barium sulphate** exhibits a marked solubility in soln. of ferric chloride which depends on the conc. of the soln. of the ferric salt; but barium sulphate is insoluble in soln. of ferric chloride containing barium chloride. The adsorption of ferric chloride by the alkaline earth sulphates was studied by N. R. Dhar and co-workers, and L. de Brouckère; and J. W. Mellor discussed the bearing of this in analytical chemistry. L. de Brouckère also studied the absorption of ferric chloride by barium sulphate; G. Lunge, the solubility of **lead sulphate** in ferric chloride soln.; M. Berthelot, the thermal change which attends the admixture of a soln. of ferric chloride with **manganese sulphate** and **ferrous sulphate**; and F. G. Berend, the action of an ethereal soln. of ferric chloride on **manganic alum.** E. M. Walton found that if the hemipentahydrate is triturated with heptahydrated ferrous sulphate, liquefaction occurs.

The action of the **alkali carbonates** on soln. of ferric chloride has been discussed in connection with the analytical reactions of iron. K. Feist observed that if the hexahydrate be triturated with powdered crystals of sodium carbonate, some bubbling occurs, carbon dioxide is evolved, and a basic ferric carbonate is formed. H. Meyer represented the reaction with **copper carbonate** by the equation:  $3\text{CuCO}_3 + 2\text{FeCl}_3 + 3\text{H}_2\text{O} = 3\text{CuCl}_2 + 2\text{Fe}(\text{OH})_3 + 3\text{CO}_2$ , the copper and chlorine are retained very tenaciously by the precipitate. H. Rose observed that **silver carbonate** precipitates the iron quantitatively as ferric hydroxide mixed with silver chloride. H. Meyer found that **calcium carbonate** precipitates ferric hydroxide quantitatively in the cold; at high temp., in a sealed tube, H. de Sénarmont, E. Stirnemann, and M. Kuhara observed that crystals of ferric oxide (*q.v.*) are formed. C. Meineke studied the analogous precipitation of ferric hydroxide with **barium carbonate**. H. Meyer found that **magnesium, zinc, and lead carbonates** also decompose an aq. soln. of ferric chloride; and N. C. Christensen discussed the solubility of lead carbonate ores in a soln. of ferric chloride. M. Kuhara obtained magnetite and hæmatite by the prolonged boiling of **siderite** or **ferrous carbonate** in a 20 per cent. soln. of ferric chloride.

**The complex salts of ferric chloride.**—J. Nicklès, and P. T. Walden observed that the tendency of the ferric halides to form complex salts with other halides increases as the at. wt. of the halogen decreases. F. G. Donnan and H. Bassett studied the tendency of ferric chloride to form complex anions. H. Remy and H. J. Rothe studied homopolar combinations with the co-ordination numbers 5 and 7; and they added that the co-ordination number of an ion represents the number of electrons which must be added to the outer sphere to bring the total up to a value which represents a stable electronic configuration.

The seventeenth-century writings of Basilius Valentinus<sup>3</sup> said that when a mixture of red vitriol and sal ammoniac is heated, a sublimate is obtained which deliquesces into an oily liquid. This product was probably a complex salt of ferric and ammonium chlorides. C. W. Scheele also obtained a complex salt of these two chlorides. P. L. Geiger, C. A. Winkler, and C. M. Marx made attempts to obtain a salt of uniform composition from mixed soln. of ammonium and ferric chlorides. They noted that the crystallizing power of the ammonium chloride

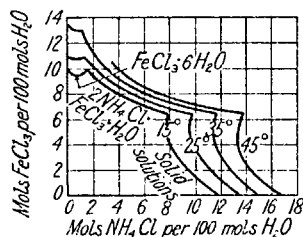


FIG. 587.—Equilibrium in the Mixed Solutions of Ammonium and Ferric Chlorides.

was favoured by the presence of ferric chloride so that instead of dendrites, cubic crystals were formed. The mixture obtained by evaporating a soln. of the two salts was for a time called *flores salis ammoniaci martiales*. O. Lehmann observed that the two salts on slow crystallization form a series of solid soln.; and this was

confirmed by J. W. Retgers. According to J. Fritzsche, the evaporation of a soln. of ammonium chloride with a large excess of ferric chloride, over sulphuric acid, furnishes red, rhombic crystals of **ammonium ferric pentachloride**, or *ammonium pentachloroferrate*,  $(\text{NH}_4)_2\text{FeCl}_5 \cdot \text{H}_2\text{O}$ , which might be mistaken for octahedra. The salt is not decomposed by water like the corresponding potassium salt. The crystals were prepared by P. T. Walden, and G. Neumann. C. Hensgen obtained it by the action of hydrogen chloride on a soln. of ammonium iron alum. F. A. Gentl observed that on evaporating the mixed soln. at  $15^\circ$  to  $20^\circ$ , regular octahedra were formed, but at  $25^\circ$  to  $40^\circ$ , these crystals are transformed into hemiprismatic crystals, which, on exposure to air, return to their original form. F. W. J. Clendinnen could not confirm the existence of this salt,  $2\text{NH}_4\text{Cl} \cdot \text{FeCl}_3 \cdot \text{H}_2\text{O}$ . R. C. Wallace discussed the salts isomorphous with  $(\text{NH}_4)_2\text{FeCl}_5 \cdot \text{H}_2\text{O}$ ; and G. Carobbi, the isomorphism of the salt with  $(\text{NH}_4)_2\text{MoCl}_5 \cdot \text{H}_2\text{O}$ . E. C. Feytis, T. Ishiwaru, and K. Honda and T. Ishiwaru gave for the magnetic susceptibility of  $2\text{NH}_4\text{Cl} \cdot \text{FeCl}_3 \cdot \text{H}_2\text{O}$  :

		-179.8°	-108.4°	-21.9°	0°	53.6°	186.0°	302.0°
$\chi \times 10^6$	.	132.7	79.5	54.3	49.9	43.2	32.6	22.8

J. L. C. Schroeder van der Kolk supposed that the solid soln. of the two salts are isomorphous mixtures of ammonium chloride with a regular modification of

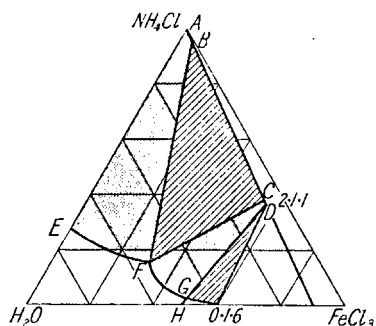


FIG. 588.—Equilibrium in the Ternary System:  $\text{NH}_4\text{Cl}$ – $\text{FeCl}_3$ – $\text{H}_2\text{O}$ , at  $25^\circ$ .

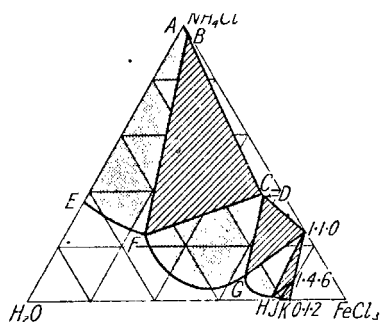


FIG. 589.—Equilibrium in the Ternary System:  $\text{NH}_4\text{Cl}$ – $\text{FeCl}_3$ – $\text{H}_2\text{O}$ , at  $60^\circ$ .

ferric chloride, possibly  $\text{FeCl}_3 \cdot 4\text{H}_2\text{O}$ ; but this hypothesis was contested by J. W. Retgers. A. Ritzel also regarded the product as a solid soln. of ammonium and ferric chlorides, and added that potassium sulphate or sodium nitrate in the soln. does not appear in the crystals. D. Balareff also discussed the subject. E. C. J. Mohr investigated the mutual solubilities at  $15^\circ$ ,  $25^\circ$ ,  $35^\circ$ , and  $45^\circ$ . Four phases were observed: (i) hydrated ferric chloride; (ii) J. Fritzsche's double salt; (iii) a series of solid soln.; and (iv) ammonium chloride. The ammonium chloride content at the triple point (1-2), and the ferric chloride at the triple point (2-3) are respectively almost unaffected by temp., so that the triple phase curves cut at about  $-15^\circ$ , probably where the double salt phase must disappear. No definite conclusions were obtained with respect to the solid soln., but they are regarded as isomorphous mixtures of ammonium chloride and J. Fritzsche's double salt. The solid soln. were discussed by A. C. D. Rivett and F. W. J. Clendinnen, G. Bruni, A. Ritzel, and W. Eitel. Olive-brown needles of **ammonium ferric tetrachloride**, or *ammonium tetrachloroferrate*,  $\text{NH}_4\text{Cl} \cdot \text{FeCl}_3$ , were prepared but they soon changed into the ordinary double salt. F. W. J. Clendinnen obtained this salt as a stable phase at  $60^\circ$ , but not at  $45^\circ$ —*vide infra*; and K. Hachmeister found that it boils at  $386^\circ$ . E. C. J. Mohr also said that the regular crystals of J. L. C. Schroeder van der Kolk are probably produced when some ammonia is present. The crystallization of soln. of ferric chloride with increasing quantities of ammonium chloride furnished isotropic, regular crystals of **ammonium ferric heptachloride**, or

*ammonium heptachlorodiferrate*,  $\text{NH}_4\text{Cl} \cdot 2\text{FeCl}_3 \cdot 4\text{H}_2\text{O}$ . F. W. J. Clendinnen could not confirm the existence of this compound at  $60^\circ$ , and E. C. J. Mohr's own data at  $45^\circ$  do not agree with the existence of this compound as a stable solid phase. The solid soln. of the compound salts were studied by K. Spangenberg and A. Neuhaus, A. Neuhaus, and D. Balareff.

H. W. B. Roozeboom observed that at  $15^\circ$ , the solid phases in mixed soln. of the two salts are hexahydrated ferric chloride, J. Fritzsche's double salt, and solid soln. of ammonium chloride, with ferric chloride rising to 7 per cent. The results are illustrated by E. C. J. Mohr's curves for  $15^\circ$ ,  $25^\circ$ ,  $35^\circ$ , and  $45^\circ$ , Fig. 587, where the first curve for soln. in equilibrium with  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , lies between the limits 9.30 to 9.93 mols  $\text{FeCl}_3$  and 0 to 1.36 mols of  $\text{NH}_4\text{Cl}$  per 100 mols of water; the second curve for soln. in equilibrium with the complex salt  $2\text{NH}_4\text{Cl} \cdot \text{FeCl}_3 \cdot \text{H}_2\text{O}$ , has the limits 9.93 to 6.8 mols  $\text{FeCl}_3$  and 1.36 to 7.8 mols  $\text{NH}_4\text{Cl}$  per 100 mols  $\text{H}_2\text{O}$ ;

TABLE XCIII.—THE TERNARY SYSTEM:  $\text{NH}_4\text{Cl}-\text{FeCl}_3-\text{H}_2\text{O}$ .

Sp. gr.	Percentage composition				Solid phases	
	Solution		Residue			
	NH <sub>4</sub> Cl	FeCl <sub>3</sub>	NH <sub>4</sub> Cl	FeCl <sub>3</sub>		
25°	1.132	24.14	7.64	87.22	2.57	Solid soln. AB
	1.327	16.05	28.97	84.36	7.36	
	1.358	16.63	30.45	31.31	46.27	B and C
	1.356	15.59	31.61	33.65	51.93	Solid soln. CD
	1.513	2.93	47.63	32.11	55.25	
	1.536	2.29	49.50	3.27	55.87	D and 0.1.6
	1.525	1.30	48.80	0.73	53.60	0.1.6
60°	1.133	31.37	7.75	79.14	3.21	Solid soln. AB
	1.268	25.40	22.95	72.34	9.45	
	1.298	24.73	25.78	38.53	42.82	B and C
	1.310	22.49	27.47	35.13	51.36	
	1.639	8.85	65.08	23.18	60.55	Solid soln. CD
	1.643	9.51	65.20	16.61	63.56	
	—	9.48	65.40	24.21	62.73	D and 1.1.0
	1.620	8.57	65.70	14.49	69.10	
	1.745	1.57	75.37	9.99	75.14	1.1.0
	—	1.15	76.31	3.55	77.54	
	—	0.25	78.10	—	—	1.4.6
	—	0.18	78.20	1.12	79.20	
	1.798	—	78.42	—	—	1.4.6 and 0.1.2
						1.2

and the third curve for soln. in the presence of the solid soln. lies between the limits 6.8 to 0 mols  $\text{FeCl}_3$  and 7.8 to 11.88 mols  $\text{NH}_4\text{Cl}$  per 100 mols of water. The soln. at the point of intersection of the two first curves is stable in presence of the hydrated ferric chloride and the double salt: that at the intersection of the second and third curves can exist in presence of the double salt and the mixed crystals containing the maximum amount of iron. The composition of the soln. at these points is independent of the quantity of the two solid phases. Whilst, however, the soln. at the first intersection is not further altered by any addition of ferric chloride, or by the addition of ammonium chloride up to the point where all the solid ferric chloride is converted into the double salt, the soln. at the second intersection is changed by the addition of one or other component, for each of these transforms one solid phase into the other. The curve for the double salt shows that this salt cannot be dissolved without undergoing decomposition. The mixed crystals contain the ferric chloride as  $\text{Fe}_2\text{Cl}_6$  with 7 to 8 mols.  $\text{H}_2\text{O}$ ; but whether as an isotropic or eolotropic admixture remains undecided. The relation between

the quantity of iron in the solid soln. mixed crystals and that in the soln. is not well known.

F. W. J. Clendinnen studied the ternary system  $\text{NH}_4\text{Cl}-\text{FeCl}_3-\text{H}_2\text{O}$  at  $25^\circ$  and  $60^\circ$ , and selections from his results at  $25^\circ$ , and  $60^\circ$  are given in Table XCIII, and plotted in Figs. 588 and 589. The difficulties attending the drying of the solid soln. near the ammonium chloride end,  $AB$ , introduce errors which explain how H. W. B. Roozeboom gave for the molar ratio  $\text{H}_2\text{O}:\text{FeCl}_3=4:1$ , and J. W. Retgers 1:1. The series of solid soln.  $CD$  have this ratio very near 1:1. For solids in equilibrium with soln. on the curve  $FG$ , both H. W. B. Roozeboom, and E. C. J. Mohr consider that the solid is 2.1.1, but the results of F. W. J. Clendinnen do not support this hypothesis, the results, indeed, show that every soln. on the solubility curve is in equilibrium with a different solid. When the proportion of ammonium chloride in the sat. soln. falls below 2.29 per cent., hexahydrated ferric chloride is the solid in equilibrium with the soln. at  $25^\circ$ . There is probably a series of solid soln. here, but it has not been detected. At  $60^\circ$ , in addition to the two series of solid soln. just indicated, three other solids appear, namely, 1.1.0, 1.4.6, and 0.1.2. E. C. J. Mohr mentioned the 1.1.0 salt,  $\text{NH}_4\text{Cl}.\text{FeCl}_3$ , and its

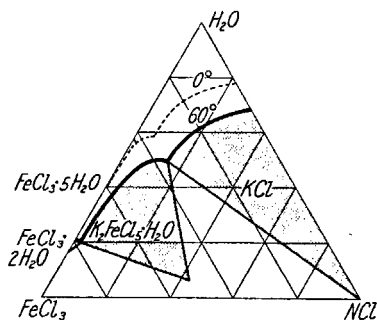


FIG. 590.—Equilibrium in the Ternary System:  $\text{KCl}-\text{FeCl}_3-\text{H}_2\text{O}$ , at  $0^\circ$  and  $60^\circ$ .

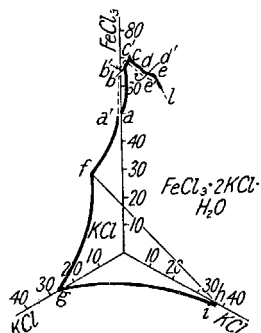


FIG. 591.—The Quaternary System:  $\text{FeCl}_3+\text{KCl}+\text{HCl}-\text{H}_2\text{O}$ , at  $25^\circ$ .

existence is here confirmed; but his salt 1.2.4 could not have been in stable equilibrium at  $45^\circ$ . The solid in equilibrium with the curve  $HJ$ , Fig. 589, was shown by F. W. J. Clendinnen to be **ammonium ferric tridecaehchloride**, or **ammonium tridecachlorotetraferate**,  $\text{NH}_4\text{Cl}.4\text{FeCl}_3.6\text{H}_2\text{O}$ . The solid in equilibrium with the soln. along  $JK$  is  $\text{FeCl}_3.2\text{H}_2\text{O}$ , and both here and in the cases of 1.1.0 and 1.4.6 salts, solid soln. are probably formed. C. E. Richards and R. W. Roberts found that the magnetic rotation of a soln. of ammonium ferric chloride of sp. gr. 1.091 is positive and there are indications of absorption bands for  $0.57\mu$  and  $0.53\mu$ .

H. Remy, and H. Remy and H. J. Rothe argued that by analogy with osmium and ruthenium, chloroferrates of the type  $[\text{FeCl}_4]'$ ,  $[\text{FeCl}_5]''$ ,  $[\text{FeCl}_6]'''$ , and  $[\text{FeCl}_7]''''$  should be possible with the chloroferrates if they are capable of existence at all. They prepared the chloroferrates of the substituted ammonium bases: **methylammonium tetraehloroferrate**,  $\{(\text{CH}_3)\text{NH}_3\}[\text{FeCl}_4]$ , melting about  $211^\circ$ ; **methylammonium heptaehloroferrate**,  $\{(\text{CH}_3)\text{NH}_3\}_4[\text{FeCl}_7]\text{H}_2\text{O}$ , melting at  $161^\circ$ ; **dimethylammonium tetraehloroferrate**,  $\{(\text{CH}_3)_2\text{NH}_2\}[\text{FeCl}_4]$ , melting at  $97^\circ$  to  $104^\circ$ ; **dimethylammonium pentaehloroferrate**,  $\{(\text{CH}_3)_2\text{NH}_2\}_2[\text{FeCl}_5]$ , melting at  $98^\circ$ ; **dimethylammonium heptaehloroferrate**,  $\{(\text{CH}_3)_2\text{NH}_2\}_4[\text{FeCl}_7]$ , melting at about  $48^\circ$ ; **trimethylammonium tetraehloroferrate**,  $\{(\text{CH}_3)_3\text{NH}\}[\text{FeCl}_4]$ ; **trimethylammonium pentaehloroferrate**,  $\{(\text{CH}_3)_3\text{NH}\}_2[\text{FeCl}_5]$ , melting at  $143^\circ$ ; **tetramethylammonium tetraehloroferrate**,  $\{(\text{CH}_3)_4\text{N}\}[\text{FeCl}_4]$ , melting above  $308^\circ$ ; **ethylammonium tetraehloroferrate**,  $\{(\text{C}_2\text{H}_5)\text{NH}_3\}[\text{FeCl}_4]$ , melting about  $85^\circ$ ; **ethylammonium heptaehloroferrate**,  $\{(\text{C}_2\text{H}_5)\text{NH}_3\}_4[\text{FeCl}_7]$ , melting at  $117^\circ$ ; **propylammonium tetraehloroferrate**,  $\{(\text{C}_3\text{H}_7)\text{NH}_3\}[\text{FeCl}_4]$ ; **propylammonium**



**heptachloroferrate**,  $\{(C_3H_7)NH_3\}_4[FeCl_7]$ , melting at  $118^\circ$  and softening at  $110^\circ$ ; and **butyl tetrachloroferrate**,  $\{(C_4H_9)NH_3\}_3[FeCl_4]$ , melting at  $60.5^\circ$ . F. Ephraim and S. Weiberg obtained black octahedra of **ammonium ferric antimony chloride**,  $9NH_4Cl \cdot 2FeCl_3 \cdot 3SbCl_4$ , from a soln. of the constituent chlorides in hydrochloric acid.

H. St. C. Deville observed that mixtures of sodium and ferric chlorides can be obtained melting to a mobile liquid at  $200^\circ$ . G. Neumann was unable to prepare

**lithium ferric chloride**; nor could **sodium ferric chloride** be prepared. F. W. Hinrichsen and E. Sachsels found that the solubility curve Fig. 592, at  $21^\circ$ , revealed the existence of a series of solid soln. of the component salts. Nor is there any evidence of the formation of a complex salt at temp. between  $3^\circ$  and  $63^\circ$ . G. Neumann came to a similar conclusion. The corresponding curves for potassium and ferric chlorides are shown in Fig. 592. They reveal the existence of a region, BC, where solid soln. are formed, and another region, AB, where the **potassium ferric pentachloroferrate**, or **potassium pentachloroferrate**,  $K_2FeCl_5 \cdot H_2O$ , is

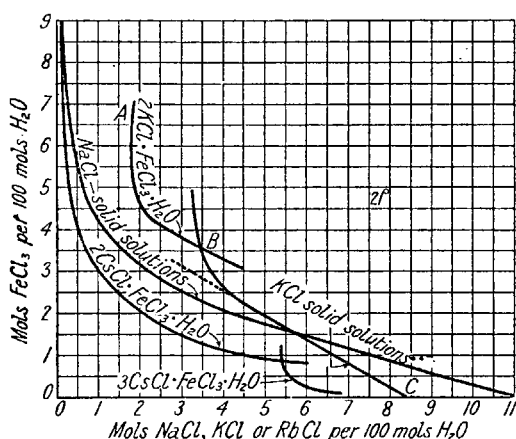


FIG. 592.—Solubility Curves of Solution of Alkali and Ferric Chlorides.

the stable solid phase. C. Hensgen obtained this salt by passing hydrogen chloride into a conc. soln. of potassium iron alum. In agreement with J. Fritzsche, and G. Neumann, but not P. T. Walden, F. W. Hinrichsen and E. Sachsels found that this salt separates from a mixed soln. of the component salts when ferric chloride is in excess. The curve CB, Fig. 592, represents the effect of ferric chloride on the solubility of the alkali chloride. G. Malquori's study of the ternary system  $KCl-FeCl_3-H_2O$ , at  $0^\circ$ , showed that with soln. containing the following percentage proportions of the constituents

KCl . . . . .	21.60	10.19	6.53	6.03	2.85	1.07	0
FeCl <sub>3</sub> . . . . .	0	16.38	27.28	35.67	58.60	42.53	4.266
Solid phase	KCl		Solid solution		2KCl.FeCl <sub>3</sub> .H <sub>2</sub> O		FeCl <sub>3</sub> .6H <sub>2</sub> O

The zone of solid soln. does not appear at  $25^\circ$  when the compositions of the soln. are :

KCl . . . . .	26.02	17.40	14.99	11.97	5.65	1.22	0
FeCl <sub>3</sub> . . . . .	0	14.90	22.14	35.88	47.27	49.33	49.76
Solid phase	KCl		2KCl.FeCl <sub>3</sub> .H <sub>2</sub> O			FeCl <sub>3</sub> .6H <sub>2</sub> O	

At  $35^\circ$ , the solid phase for ferric chloride is the pentahydrate, and at  $60^\circ$  the dihydrate :

KCl . . . . .	31.30	16.30	14.41	4.96	2.25	1.90	0
FeCl <sub>3</sub> . . . . .	0	28.73	36.78	53.98	74.08	77.13	78.86
Solid phase	KCl		2KCl.FeCl <sub>3</sub> .H <sub>2</sub> O			FeCl <sub>3</sub> .2H <sub>2</sub> O	

G. Malquori studied the quaternary system:  $\text{FeCl}_3\text{-KCl-HCl-H}_2\text{O}$  at  $25^\circ$ , and he found that:

PERCENTAGE COMPOSITION OF SOLUTION				SOLID PHASES
KCl	$\text{FeCl}_3$	HCl	$\text{H}_2\text{O}$	
11.97	35.88	—	52.15	KCl, and $\text{FeCl}_3 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$
1.50	1.15	39.20	58.15	ditto.
1.22	49.33	—	49.45	$\text{FeCl}_3 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$
—	67.13	1.48	31.39	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 3\frac{1}{2}\text{H}_2\text{O}$
1.10	66.91	1.27	30.72	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , $\text{FeCl}_3 \cdot 3\frac{1}{2}\text{H}_2\text{O}$ , and $\text{FeCl}_3 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$
—	69.93	3.96	26.11	$\text{FeCl}_3 \cdot 3\frac{1}{2}\text{H}_2\text{O}$ , and $\text{FeCl}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$
1.15	69.10	3.15	26.60	$\text{FeCl}_3 \cdot 3\frac{1}{2}\text{H}_2\text{O}$ , $\text{FeCl}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ , and $\text{FeCl}_3 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$
—	69.47	8.63	21.90	$\text{FeCl}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ , and $\text{FeCl}_3 \cdot 2\text{H}_2\text{O}$
1.27	68.87	8.20	21.66	$\text{FeCl}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ , $\text{FeCl}_3 \cdot 2\text{H}_2\text{O}$ , and $\text{FeCl}_3 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$
—	70.30	12.30	17.40	$\text{FeCl}_3 \cdot 2\text{H}_2\text{O}$ , and $\text{FeCl}_3 \cdot \text{HCl} \cdot 2\text{H}_2\text{O}$
1.71	70.10	11.85	16.34	$\text{FeCl}_3 \cdot 2\text{H}_2\text{O}$ , $\text{FeCl}_3 \cdot \text{HCl} \cdot 2\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$

The results are plotted in Fig. 591. The point *h* represents a soln. sat. with HCl; *f*, one sat. with KCl and  $\text{FeCl}_3 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$ . The points *b'c'd'e'* refer to data of H. W. B. Roozeboom for the hydrates of ferric chloride. The region *fghi* represents a soln. sat. with KCl; *hfa'b'c'd'e'*, one sat. with  $\text{FeCl}_3 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$ ; *aa'bb'*, one sat. with  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ; *bb'cc'*, one sat. with  $\text{FeCl}_3 \cdot 3\frac{1}{2}\text{H}_2\text{O}$ ; *cc'dd'*, one sat. with  $\text{FeCl}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ ; *dd'ee'*, one sat. with  $\text{FeCl}_3 \cdot 2\text{H}_2\text{O}$ ; and *ee'l*, one sat. with  $\text{FeCl}_3 \cdot \text{HCl} \cdot \text{H}_2\text{O}$ . J. Fritzsche, and C. Hensgen prepared red crystals of this salt; and G. Neumann obtained it in reddish-brown octahedra and rhombic dodecahedra by adding potassium chloride to a hot, conc. soln. of ferric chloride in hydrochloric acid of sp. gr. 1.19. R. C. Wallace discussed the salts which are isomorphous with  $\text{K}_2\text{FeCl}_5 \cdot \text{H}_2\text{O}$ ; and G. Carobbi, the isomorphism of  $\text{R}_2\text{FeCl}_5 \cdot \text{H}_2\text{O}$  with  $\text{R}_2\text{MoCl}_5 \cdot \text{H}_2\text{O}$ , where  $\text{R}=\text{NH}_4$  or K. According to F. W. Hinrichsen and E. Sachsels, the temp. of formation from its components is  $22^\circ$  to  $22.5^\circ$ ; and unlike J. Fritzsche, and P. T. Walden, they did not find the salt to be deliquescent, nor were they able to confirm A. Werner's product  $3\text{KCl} \cdot \text{FeCl}_3$ . O. Stelling and F. Olsson studied the X-ray spectrum of the pentachloride.

G. and P. Spacu observed the formation of the **potassium ferric ammino-chlorides**,  $\text{K}_2[\text{FeCl}_5] \cdot 11\text{NH}_3$  with the vap. press. 145 mm. at  $-30^\circ$ , and the heat of formation 8.83 Cals. per mol of  $\text{NH}_3$ ;  $\text{K}_2[\text{FeCl}_5] \cdot 6\text{NH}_3$ —with the vap. press. 37, 37, and 39 mm., respectively, at  $0^\circ$ ,  $14.9^\circ$ , and  $34.8^\circ$ , and the heat of formation 11.75 Cals. per mol of  $\text{NH}_3$ ;  $\text{K}_2[\text{FeCl}_5] \cdot 6\text{NH}_3$ —with the vap. press.  $p=47$  mm. at  $78^\circ$ , and the heat of formation 15.51 Cals. per mol of  $\text{NH}_3$ ; and  $\text{K}_2[\text{FeCl}_5] \cdot 2\text{NH}_3$ —with the vap. press. 7 and 2 mm. for the salt, respectively, with 2.15 and 2.06 mols  $\text{NH}_3$ , at  $120^\circ$ .

P. T. Walden prepared **rubidium ferric pentachloride**, or *rubidium pentachloroferrate*,  $\text{Rb}_2\text{FeCl}_5 \cdot \text{H}_2\text{O}$ , by crystallization from a soln. containing 50 grms. of rubidium chloride and 10 grms. of ferric chloride. The rhombic crystals are easily soluble in water, and are identical with those to which R. Godefroy assigned the formula  $\text{Rb}_3\text{FeCl}_6$ . The salt  $\text{Rb}_2\text{FeCl}_5 \cdot \text{H}_2\text{O}$ , was first prepared by G. Neumann in small yellow crystals by adding the alkali chloride to a hot, conc. soln. of ferric chloride in hydrochloric acid of sp. gr. 1.19. P. T. Walden prepared **cæsium ferric pentachloride**, or *cæsium pentachloroferrate*,  $\text{Cs}_2\text{FeCl}_5 \cdot \text{H}_2\text{O}$ , and also **cæsium ferric hexachloride**, or *cæsium hexachloroferrate*, by crystallization from aq. soln. of the component salts. F. W. Hinrichsen and E. Sachsels's observations on the range of stability of these two salts in aq. soln. are illustrated in Fig. 592. O. Stelling and F. Olsson studied the X-ray spectrum of the pentachloride. P. T. Walden described **cæsium ferric tetrachloride**, *cæsium tetrachloroferrate*,  $\text{CsFeCl}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ , but F. W. Hinrichsen and E. Sachsels were unable to confirm its existence. E. H. Duclaux reported **cæsium ferric octochloride**,  $2\text{FeCl}_3 \cdot 2\text{CsCl} \cdot \text{H}_2\text{O}$ ; **cæsium ferric decachloride**,  $2\text{FeCl}_3 \cdot 4\text{CsCl} \cdot 2\text{H}_2\text{O}$ ; and **cæsium ferric dodecachloride**,  $2\text{FeCl}_3 \cdot 6\text{CsCl} \cdot 2\text{H}_2\text{O}$ , but their existence has not been confirmed.

According to G. Herrmann, the crystallization of an aq. soln. of cuprous and

ferric chlorides furnishes green crystals of **cuprous ferric tetrachloride**, or *cuprous tetrachloroferrate*,  $\text{CuFeCl}_4 \cdot 4\text{H}_2\text{O}$ . Besides the *tetrahydrate*, the anhydrous salt can be obtained by fusion. The thermal diagram, Fig. 593, shows that the anhydrous salt melts at  $320^\circ$ , and there are two eutectics at  $306^\circ$  and  $263^\circ$  with respectively 50 and 88 per cent. of ferric chloride. H. Meyer observed that when basic copper chloride is dissolved in a soln. of ferric chloride, a precipitate of hydrated ferric oxide, contaminated with copper and chlorine, is formed. O. Lehmann studied solid soln. of ferric, cupric, and ammonium chlorides. G. Neumann could not prepare **silver ferric chloride**; G. Neumann could not prepare **calcium, strontium, or barium ferric chlorides**. I. Baschiloff and J. Wilniansky found that barium chloride can be salted out of its aq. soln. by ferric chloride. G. Malfitano and L. Michel discussed the effect of barium chloride on the hydrolysis of ferric chloride. J. W. Retgers studied the solid soln. of silver and ferric chlorides. He obtained **beryllium ferric pentachloride**, or *beryllium pentachloroferrate*,  $\text{BeFeCl}_5 \cdot \text{H}_2\text{O}$ , in small, orange-yellow crystals, by adding

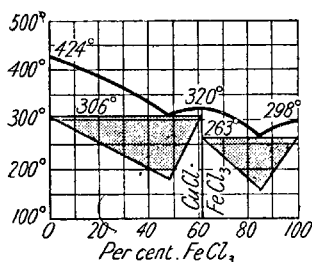


FIG. 593.—Freezing-point Curves of the System:  $\text{CuCl}-\text{FeCl}_3$ .

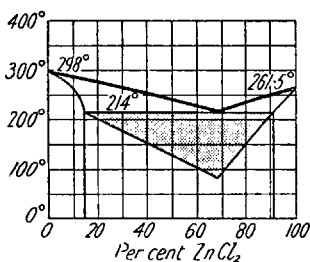


FIG. 594.—Freezing-point Curves of the System:  $\text{ZnCl}_2-\text{FeCl}_3$ .

beryllium chloride to a hot, conc. soln. of ferric chloride in hydrochloric acid of sp. gr. 1.19, he also obtained large, brownish-yellow, hygroscopic crystals of **magnesium pentachloride**, or *magnesium pentachloroferrate*,  $\text{MgFeCl}_5 \cdot \text{H}_2\text{O}$ ; but he could not prepare **zinc ferric chloride**, and **cadmium ferric chloride** by this process. G. Malfitano and L. Michel discussed the effect of magnesium chloride on the hydrolysis of ferric chloride; and I. I. Saslawsky studied the changes in vol. on mixing soln. of ferric and magnesium chlorides. G. Herrmann found that zinc and ferric chlorides have a eutectic at  $214^\circ$  with 70 per cent. of zinc chloride—Fig. 594—and that solid soln. are formed at both ends of the series. G. Malfitano and L. Michel discussed the effect of mercuric chloride on the hydrolysis of ferric chloride. G. Malquori studied the ternary system:  $\text{AlCl}_3-\text{FeCl}_3-\text{H}_2\text{O}$  at  $25^\circ$ , but found neither compound—**aluminium ferric chloride**—nor solid soln.—Fig. 599. When associated with potassium chloride, G. Malquori observed:

PERCENTAGE COMPOSITION OF SOLUTION

KCl	$\text{AlCl}_3$	$\text{FeCl}_3$	$\text{H}_2\text{O}$
11.97	—	35.88	52.15
2.0	29.21	3.00	67.79
1.22	—	49.33	49.45
6.50	10.80	38.50	44.20
—	5.21	38.25	55.54
3.91	30.15	—	65.94

SOLID PHASES

KCl, and $\text{FeCl}_3 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$
KCl, $\text{FeCl}_3 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$ , and $\text{AlCl}_3 \cdot \text{H}_2\text{O}$
$\text{FeCl}_3 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$ , and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$
$\text{FeCl}_3 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$ , $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ .
$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , and $\text{AlCl}_3 \cdot \text{H}_2\text{O}$
KCl, and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$

The results are plotted in Fig. 595. The point *e* represents soln. sat. with  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{FeCl}_3 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$ , and  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ; and *i*, soln. sat. with  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ , KCl, and  $\text{FeCl}_3 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$ . The region *fgie* represents soln. sat. with KCl; *bcei*, soln. sat. with  $\text{FeCl}_3 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$ ; *abed*, with  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ; and *edihg*, with  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ . In the case of the quinquinary system:  $\text{FeCl}_3-\text{AlCl}_3-\text{KCl}-\text{HCl}-\text{H}_2\text{O}$  at  $25^\circ$ , it was observed that:

PERCENTAGE COMPOSITION OF SOLUTION				
$\text{FeCl}_3$	$\text{AlCl}_3$	$\text{KCl}$	$\text{HCl}$	$\text{H}_2\text{O}$
—	0.09	1.18	33.21	65.52
3.0	29.21	2.0	—	65.79
0.98	0.25	1.87	38.25	58.65
1.15	—	1.50	39.20	58.15
38.50	10.80	6.50	—	44.20
69.91	1.31	1.01	11.0	16.77
69.81	1.02	—	11.75	17.42
70.01	—	1.71	11.85	16.34

## SOLID PHASES

$\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ , and  $\text{KCl}$   
 $\text{FeCl}_3 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$ ,  $\text{KCl}$ , and  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$   
 $\text{FeCl}_3 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$ ,  $\text{KCl}$ , and  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$   
 $\text{FeCl}_3 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$ , and  $\text{KCl}$   
 $\text{FeCl}_3 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$ ,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , and  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$   
 $\text{FeCl}_3 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$ ,  $\text{FeCl}_3 \cdot \text{HCl} \cdot 2\text{H}_2\text{O}$ ,  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ,  
 and  $\text{FeCl}_3 \cdot 2\text{H}_2\text{O}$   
 $\text{FeCl}_3 \cdot \text{HCl} \cdot 2\text{H}_2\text{O}$ ,  $\text{FeCl}_3 \cdot 2\text{H}_2\text{O}$ , and  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ .  
 $\text{FeCl}_3 \cdot \text{HCl} \cdot 2\text{H}_2\text{O}$ ,  $\text{FeCl}_3 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$ , and  $\text{FeCl}_3 \cdot 2\text{H}_2\text{O}$

The results are plotted in Fig. 596. The area *aelm* represents soln. sat. with  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{KCl}$ ; *ebmn*, with  $\text{KCl}$  and  $\text{FeCl}_3 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$ ; *mefg*, with  $\text{FeCl}_3 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$  and  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ; *fdgh*, with  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ , and solids of the system  $\text{FeCl}_3$ - $\text{HCl}$ - $\text{H}_2\text{O}$ ; and *iefg*, with  $\text{FeCl}_3 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$ , and solids of the system  $\text{FeCl}_3$ - $\text{HCl}$ - $\text{H}_2\text{O}$ . G. Neumann, and F. Wöhler and A. Ahrens reported red, prismatic crystals of thalious ferric chloride to be formed from aq. soln. of the component salts, but they are decomposed by water. According to G. Scarpa, when a mixture

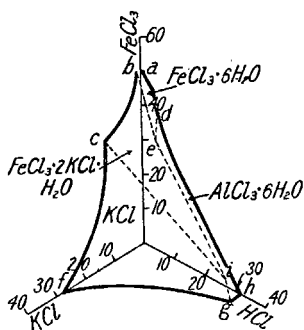


FIG. 595.—The Quaternary System :  $\text{FeCl}_3$ - $\text{AlCl}_3$ - $\text{KCl}$ - $\text{H}_2\text{O}$  at  $25^\circ$ .

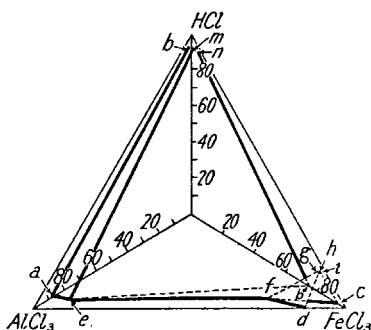


FIG. 596.—The Quinquenary System :  $\text{FeCl}_3$ - $\text{AlCl}_3$ - $\text{KCl}$ - $\text{HCl}$ - $\text{H}_2\text{O}$  at  $25^\circ$ .

of the thalious and ferric chlorides is fused, some of the latter is volatilized, and the thermal diagram could not be completed when more than 62 molar per cent. is present. The diagram, Fig. 597, shows that there is a eutectic at  $266^\circ$  with 26 molar per cent. of ferric chloride and a maximum at  $290^\circ$  corresponding with **thalious ferric pentachloride**, or **thalious pentachloroferrate**,  $\text{Ti}_2\text{FeCl}_5$ , which is stable on fusion. There is another eutectic at  $220^\circ$ . With high proportions of ferric chloride, crystallization sets in only at a relatively high temp., so that with

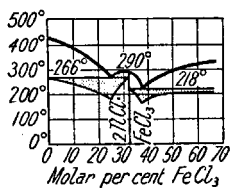


FIG. 597.—Freezing-point Curves of the System :  $\text{TiCl}_3$ - $\text{FeCl}_3$ .

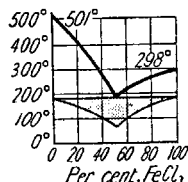


FIG. 598.—Freezing-point Curves of the System :  $\text{FeCl}_3$ - $\text{PbCl}_2$ .

62 per cent. ferric chloride, crystallization begins at  $299^\circ$  which is near the m.p. of ferric chloride. It is hence inferred that there is a second maximum beyond this temp. G. Neumann was unable to prepare **lead ferric chloride**, and **manganous ferric chloride** in acidic soln. G. Herrmann observed that lead and ferric chlorides have a eutectic at  $178^\circ$  with 50 per cent. of ferric chloride—Fig. 598. K. Johansson observed a mineral of the composition  $\text{Pb}(\text{Cl},\text{OH})_2 \cdot 4\text{PbO} \cdot 2\text{Fe}_2\text{O}_3$ , at Jacobsberg, Sweden. It was called **hæmatophanite**, in allusion to its dark reddish-brown colour

—thin plates are blood-red. The crystals are tetragonal with the axial ratio  $a:c=1:1.95$ . The sp. gr. is 7.70; the hardness 2 to 3; and the optical character is negative. The cleavage is micaceous. For the complex with antimony pentachloride, *vide supra*.

According to J. Lefort,<sup>4</sup> **ferrosic chloride**,  $\text{Fe}_3\text{Cl}_8.18\text{H}_2\text{O}$ , or  $\text{FeCl}_2.2\text{FeCl}_3.18\text{H}_2\text{O}$ —according to H. Chandra, the formula should be  $\text{Fe}_3\text{Cl}_8.10\text{H}_2\text{O}$ —is formed when

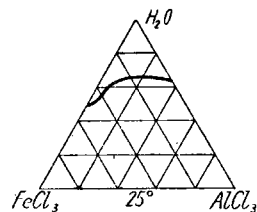


FIG. 599.—Equilibrium in the Ternary System:  $\text{AlCl}_3\text{--FeCl}_3\text{--H}_2\text{O}$  at  $25^\circ$ .

ferric oxide is dissolved in conc. hydrochloric acid, and the soln. evaporated over conc. sulphuric acid. The yellow, crystalline mass is very deliquescent, it melts at  $48^\circ$ ; loses water at  $50^\circ$ , and hydrogen chloride at  $90^\circ$ . G. Neumann doubted the existence of this salt, but H. Chandra confirmed J. Lefort's deductions. J. W. Retgers observed no evidence of the formation of solid soln. when a mixed soln. of ferrous and ferric chlorides is crystallized; and H. Remy and H. J. Rothe observed no sign of the formation of a double salt. According to A. Werner's coordination scheme, the salt is formulated  $\text{Fe}''[\text{Fe}'''\text{Cl}_4]_2$ , and the decahydrate,  $[\text{Fe}''(\text{H}_2\text{O})_6][\text{Fe}'''\text{Cl}_4].4\text{H}_2\text{O}$ .

C. Hensgen reported an intermediate chloride,  $\text{Fe}_3\text{Cl}_4.5\text{H}_2\text{O}$ , to be formed in green needles by dissolving ferrous sulphate in conc. hydrochloric acid, and treating the soln. with hydrogen chloride and air. H. Chandra also obtained a product  $\text{Fe}_3\text{Cl}_7.10\text{H}_2\text{O}$ , by evaporating in the absence of air a hydrochloric acid soln. of the basic carbonate  $\text{NH}_4[\text{Fe}_2'''\text{Fe}''.(\text{CO}_3)_3\text{O}]2\text{H}_2\text{O}$ . He said that the salt is the chloride of a base  $\text{Fe}_2'''\text{Fe}''(\text{OH})_7.n\text{H}_2\text{O}$ .

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### § 38. The Iron Bromides

Iron forms **ferrous bromide**,  $\text{FeBr}_2$ , and **ferric bromide**,  $\text{FeBr}_3$ , and their hydrates; and there is also a **ferrosic bromide**,  $\text{Fe}_3\text{Br}_8$ , and its hydrates; as well as a mixed chlorobromide. According to P. Höfer,<sup>1</sup> the commercial iron bromide approximates in composition to ferrosic bromide,  $\text{Fe}_3\text{Br}_8 \cdot n\text{H}_2\text{O}$ , but with rather less than this proportion of bromine. Its preparation and properties were described by K. Kubierschky, F. Chemnitius, and W. Hüttner.

**The preparation of ferrous bromide.**—According to J. B. Berthelot, bromine does not act on iron in the cold, but, as shown by C. Löwig, J. von Liebig, and J. B. Berthelot, if iron be heated to dull redness in bromine, **ferrous bromide**,  $\text{FeBr}_2$ , is formed, and it solidifies to a yellow, crystalline mass. A. Scheufelen said that the anhydrous bromide is most readily prepared by passing a current of carbon dioxide and bromine vapour through a hot porcelain tube containing metallic iron. Ferrous bromide sublimes forming greenish-yellow scales, which deliquesce on exposure to air. A. E. Nordenskjöld obtained ferrous bromide by passing hydrogen bromide over heated iron; and G. P. Baxter and co-workers heated iron in a current of dry nitrogen and hydrogen bromide at a temp. high enough to sublime the product. The product was contaminated by some phosphate—derived possibly from an impurity in the hydrogen bromide. The sublimate was heated in a current of dry nitrogen and hydrogen bromide until it showed no trace of ferric bromide when tested with ammonium thiocyanate. The anhydrous salt can also be obtained by heating one of the hydrates in a current of nitrogen and hydrogen bromide at about  $400^\circ$ . F. Chemnitius, and A. Ferrari and F. Giorgi used this process; and W. Biltz and G. F. Hüttig added that the temp. of dehydration must be kept low. W. Biltz and E. Birk recommended purifying the salt by resublimation in a current of hydrogen bromide. C. Löwig said that ferrous bromide is formed when iron filings are heated with ammonium bromide, when ammonia and hydrogen are evolved. L. Hackspill and R. Grandadam obtained ferrous bromide by heating an alkali bromide with iron at a high temp.:  $\text{Fe} + 2\text{NaBr} = 2\text{Na} + \text{FeBr}_2$ . P. Höfer obtained ferrous bromide by heating hydrated ferrosic bromide to  $400^\circ$  or  $500^\circ$  in the absence of air; and W. Hieber and G. Bader obtained it by the photochemical



decomposition of ferrous tetracarbonyl bromide. F. W. Bergstrom obtained the salt by the action of a soln. of ammonium bromide in liquid ammonia on iron wire.

**The hydrates of ferrous bromide.**—According to C. Löwig, an aq. soln. of ferrous bromide is formed when the anhydrous salt is dissolved in water; and when iron is dissolved in bromine water, or in hydrobromic acid. Similar processes were employed by J. B. Berthemot, C. Chojnacky, H. Lescœur, J. H. Long, F. A. Volkmann, and C. R. A. Wright and C. Thompson. When the aq. soln. is evaporated, it deposits crystals of the *hexahydrate*,  $\text{FeBr}_2 \cdot 6\text{H}_2\text{O}$ . A. Étard found the percentage solubility,  $S$ , of ferrous bromide in water to be:

	-20°	0°	10°	20°	30°	40°	60°	80°	100°
$S$	47.0	50.3	52.4	53.5	55.0	56.2	59.0	61.5	64.0

According to F. A. Volkmann, the solid phase between 10° and 47° is the hexahydrate, and above 47°, the *tetrahydrate*,  $\text{FeBr}_2 \cdot 4\text{H}_2\text{O}$ , so that the transition point is 47°. If the conc. soln. approximating  $\text{FeBr} + 9.5\text{H}_2\text{O}$ , be cooled to -10° to 30°, small, green, silky crystals of the hexahydrate are formed. F. Schimmel studied the solubility curves of ferrous bromide, and found for the solubility  $S$  grms. of  $\text{FeBr}_2$  in 100 grms. of soln.

	-6.1°	-25.0°	-43.6°	-37.0°	-29.3°	30°	49.0°	57°	83.0°	132.0°
$S$	18.5	35.2	42.25	43.5	47.65	55.4	58.45	58.8	63.3	70.2
	Ice		$\text{FeBr}_2 \cdot 9\text{H}_2\text{O}$		$\text{FeBr}_2 \cdot 6\text{H}_2\text{O}$		$\text{FeBr}_2 \cdot 4\text{H}_2\text{O}$		$\text{FeBr}_2 \cdot 2\text{H}_2\text{O}$	

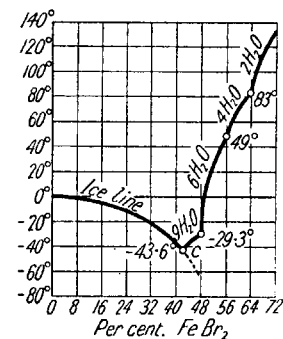
The results are plotted in Fig. 600. The eutectic temp. is -43.6° with 42.25 per cent. of ferrous bromide. There is a transition temp. at -29.3° corresponding

with the passage of the enneahydrate,  $\text{FeBr}_2 \cdot 9\text{H}_2\text{O}$ , to the hexahydrate. The hexahydrate was studied by J. B. Berthemot, J. Eggert and J. Reitstötter, H. Lescœur, C. Löwig, and F. A. Volkmann. F. Schimmel found that at 49°, the hexahydrate passes to the tetrahydrate studied by G. P. Baxter and co-workers, and F. A. Volkmann. F. Schimmel found that the tetrahydrate passes to the dihydrate,  $\text{FeBr}_2 \cdot 2\text{H}_2\text{O}$ , at 83°. H. Lescœur's measurements of the vap. press. also agreed with the existence of the dihydrate, as well as of a *monohydrate*,  $\text{FeBr}_2 \cdot \text{H}_2\text{O}$ .

**The physical properties of ferrous bromide.**—

J. von Liebig, C. Löwig, and A. Scheufelen said that the **colour** of the salt crystallized from the molten state is greenish-yellow; W. Biltz and G. F. Hüttig said the salt obtained from the dehydration of the hydrate

FIG. 600.—The Solubility of Ferrous Bromide in Water.



is ochre-yellow; G. P. Baxter and co-workers said the colour of the salt is light yellow or dark brown. F. Schimmel said that all the hydrates of ferrous bromide are green, and that the "red, hygroscopic powder" of commerce owes its colour to contamination with ferric bromide. W. Biltz and E. Birk said that the sublimed salt forms yellow, transparent scales; A. E. Nordenskjöld found that the sublimed **crystals** are white, six-sided, hexagonal, and uniaxial. A. Ferrari and F. Giorgi observed that the **X-radiogram** corresponds with a hexagonal space-lattice of the cadmium iodide type, being composed of three orthogonal prisms with rhombic bases, each containing a mol. of  $\text{FeBr}_2$ . The parameters  $a=3.740 \text{ \AA}$ , and  $c=6.171 \text{ \AA}$ , or  $a:c=1:1.65$ . W. Hieber and E. Levy studied the lattice energy. G. P. Baxter found the **specific gravity** to be 4.636 at 25°/4°; W. Biltz and E. Birk gave 4.624 at 25°/4°; and A. Ferrari and F. Giorgi calculated 4.790 from the vol. of the elementary cell. W. Biltz gave 46.65 for the mol. vol. at 25°; F. Ephraim and co-workers, W. Biltz, and I. I. Saslawsky studied the change in vol. which attends the formation of the

compound from its elements. A. Heydweiller found that soln. with  $C$  mol of  $\text{FeBr}_2$  per litre have a sp. gr. at  $18^\circ/4^\circ$ , reduced to a vacuum:

$C$ . . . . .	0.25	0.50	1.0	1.5	2.0	2.5
Sp. gr. . . . .	1.04692	1.0932	1.1850	1.2756	1.3660	1.4560

F. Schimmel found that the **boiling-point** of a sat. soln., with 70.2 per cent. of  $\text{FeBr}_2$ , is  $132^\circ$ ; and H. Lescœur gave for the **vapour pressure**,  $p$  mm., of the sat. soln.:

	$40^\circ$	$50^\circ$	$60^\circ$	$70^\circ$	$80^\circ$	$90^\circ$
$p$ . . . . .	24	33	53	85	118	180

For the vap. press. of the dihydrate at  $110^\circ$ ,  $120^\circ$ , and  $210^\circ$ , he gave 90, 120, and 210 mm. respectively; and for the monohydrate at  $160^\circ$ ,  $p=195$  mm. C. Löwig, and A. Scheufelen observed that the salt melts and volatilizes at a high temp. A. Ferrari and F. Giorgi gave  $684^\circ$  for the **melting-point** of the anhydrous salt. A. Ferrari discussed the relation between the m.p. and the space-lattice. The **transition-points** of the different hydrates are indicated above; and J. Eggert and J. Reitstötter discussed the transition:  $\text{FeBr}_2 \cdot 6\text{H}_2\text{O} \rightleftharpoons \text{FeBr}_2 \cdot 4\text{H}_2\text{O} + 2\text{H}_2\text{O}$  in soln. M. Berthelot gave for the **heat of formation**  $(\text{Fe}, \text{Br}_{2\text{gas}}, \text{Aq.})=85.9$  Cals., and  $(\text{Fe}, \text{Br}_{2\text{liq.}}, \text{Aq.})=78.5$  Cals.; J. Thomsen, 78.07 at  $18^\circ$ ; W. Hieber and A. Woerner, 59.87 Cals.; and T. Andrews, 80.8 Cals. J. Thomsen gave  $(\text{Fe}, 2\text{HBr}, \text{Aq.})=24.81$  Cals. Observations were also made by P. A. Favre and J. T. Silbermann. F. Ephraim and O. Schütz discussed some relationships of the heat of formation. J. Thomsen measured the heat of soln. of iron in hydrobromic acid; and M. Berthelot, the heat of neutralization. G. Beck studied the **free energy** and the **entropy** of the salt. W. Hieber and E. Levy studied the **lattice energy** of the crystals.

G. Limann measured the **index of refraction** of aq. soln. of  $C$  eq. of ferrous bromide per litre, and obtained:

$C$ . . . . .	0	0.5	1.0	2.0	4.0	5.0
$\mu \begin{cases} H_\alpha . . . . . \\ D . . . . . \\ H\beta . . . . . \\ H\gamma . . . . . \end{cases}$	1.33139 1.33322 1.33737 1.34060	1.34042 1.34237 1.34681 1.35032	1.34931 1.35137 1.35609 1.35982	1.36679 1.36910 1.37439 —	1.40043 1.40314 1.41035 —	1.41686 1.41982 1.42671 —

Observations were also made by A. Heydweiller, who also gave for the **molecular refraction** of conc. up to  $5N$ - $\text{FeBr}_2$ , 26.10; and G. Limann, 26.06 on the  $\mu^2$ -formula at  $18^\circ$  with Na-light. There is a small increase in the **dispersion** with decreasing concentration. A. Heydweiller gave for the eq. **electrical conductivity** of soln.,  $\lambda$  mho, with an eq. of  $\text{FeBr}_2$  per litre, at  $18^\circ$ :

$C$ . . . . .	0.5	1.0	2.0	3.0	4.0	5.0
$\lambda$ . . . . .	72.3	64.3	50.0	41.94	33.65	26.25

with the limiting value  $\lambda_\infty=113$  at  $18^\circ$ . G. Limann discussed the relations between the electrical conductivity and the refraction of the soln. W. Isbekoff measured the decomposition potential of soln. of ferrous bromide in fused zinc bromide. L. Pauling and M. L. Huggins studied the magnetic properties.

**The chemical properties of ferrous bromide.**—G. P. Baxter observed that when anhydrous ferrous bromide is heated in moist **hydrogen**, it is slowly reduced; the reduction is complete at a high temp. The anhydrous salt is stable in dry **air**; but in ordinary air, A. Scheufelen observed that the salt gradually acquires a brown crust; and is deliquescent. C. Löwig observed that when heated in air, some of the salt volatilizes, and some ferric oxide is formed, but P. Höfer was unable to detect the formation of ferric bromide. C. Löwig, and G. P. Baxter and co-workers observed that the aq. soln. is oxidized by air, becoming darker in colour, and depositing a basic salt; H. Lescœur added that the bromide soln. oxidizes more rapidly than the chloride soln. C. Löwig observed that **water** vapour at a red-heat converts ferrous bromide into hydrogen bromide and ferric oxide.

The solubility in water is discussed above. J. H. Long found that the degree of **hydrolysis** of 0.54*N*-FeBr<sub>2</sub>, calculated from the rate of inversion of cane-sugar, is 0.109 per cent. G. J. Fowler observed that ferrous bromide is decomposed when heated in **ammonia**, as in the case with ferrous chloride. Ammonia is absorbed by ferrous bromide forming hexa-, di-, and monoamines. The ranges of existence observed by W. Biltz and co-workers are summarized in Fig. 601. W. Biltz and

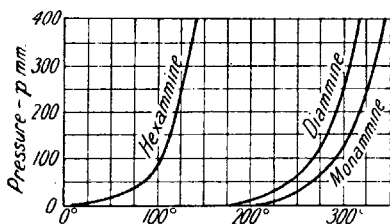


FIG. 601.—Dissociation Pressures of the Amines of Ferrous Bromide.

W. Hieber and G. Bader obtained it by passing tetracarbonyl dibromide over iron; and E. Weitz and H. Müller, by the action of ammonium bromide on an ammoniacal soln. of ferrous hexamminoacetate, or by passing ammonia into a soln. of 5 grms. of hexahydrated ferrous bromide and 10 grms. of ammonium bromide in 25 c.c. of water. The salt prepared dry is a voluminous white powder, and when prepared by the wet process it forms pale-green octahedra which, according to W. Biltz, belong to the cubic system; and the space-lattice has the parameter  $a=10.51$  Å., with the atoms Br, and Fe, and the molecule NH<sub>3</sub> arranged as in the hexamminochloride. G. B. Naess and O. Hassel studied the sphere of action of the anion. W. Biltz and E. Birk found the sp. gr. to be 1.812 at 25°/4°, so that it occupies about 2.76 times the vol. of the salt free from ammonia. The dissociation press.,  $p$  mm., was measured by F. Ephraim, and W. Biltz and co-workers, and the results are summarized in Fig. 601.

	63°	84.5°	105.5°	115.3°	130°	149°	153°
$p$	22	48	114	175	329	683	775

F. Müller gave 44° to 149° for the dissociation temp. G. Beck gave 478 cal. for the heat of formation. W. Biltz, and W. Biltz and G. F. Hüttig gave for the heat of formation, FeBr<sub>2</sub>+6NH<sub>3gas</sub>=94.02 Cals., or 15.67 Cals.—F. Ephraim gave 14.9 Cals.—per mol of ammonia; and FeBr<sub>2</sub>.2NH<sub>3</sub>+4NH<sub>3gas</sub>=53.35 Cals., or 13.34 Cals. per mol of ammonia. The free energy of the reaction FeBr<sub>2</sub>+6NH<sub>3gas</sub>=FeBr<sub>2</sub>.6NH<sub>3</sub>, at 27°, is 37.14 Cals., or 6.19 Cals. per mol of ammonia. W. Biltz and co-workers showed that salt is a hexamine-cation, [Fe(NH<sub>3</sub>)<sub>6</sub>]Br<sub>2</sub>. F. Ephraim added that the salt is oxidized by air more slowly than the hexamminochloride. F. W. Bergstrom also made some observations. According to F. Ephraim, and W. Biltz and G. F. Hüttig, when the hexamine is heated, it forms **ferrous diamminobromide**, FeBr<sub>2</sub>.2NH<sub>3</sub>, which, at 215°, 230°, and 277°, has the respective dissociation press. 11.5, 23.5, and 126 mm., and the respective heats of dissociation, 21.9, 21.9, and 22.3 Cals.; and F. Müller gave over 300° for the dissociation temp. W. Biltz found that the heat of formation FeBr<sub>2</sub>+2NH<sub>3gas</sub>=40.65 Cals., or 20.32 Cals. per mol of ammonia; and FeBr<sub>2</sub>.NH<sub>3</sub>+NH<sub>3</sub>=19.87 Cals. The free energy of the reaction FeBr<sub>2</sub>+2NH<sub>3gas</sub>=FeBr<sub>2</sub>.2NH<sub>3</sub>, at 27°, is 21.18 Cals. or 10.59 Cals. per mol of ammonia. W. Biltz observed that the anion is co-ordinated in the complex, and unlike the hexamine, the diammine is a molecular compound. W. Hieber and E. Levy studied the energy of formation. F. Ephraim, and W. Biltz and G. F. Hüttig showed that the diammine forms **ferrous aminobromide**, FeBr<sub>2</sub>.NH<sub>3</sub>, as a dark grey mass, which, at 215°, 230°, and 277°, has the respective dissociation press. 5.7, 9.7, and 61.5 mm., and the respective heats of dissociation

22.6; 22.8, and 23.1 Cals. W. Biltz observed that the heat of formation  $\text{FeBr}_2 + \text{NH}_{3\text{gas}} = 20.78$  Cals.; and the free energy of formation, at  $27^\circ$ , is 11.08 Cals. The complex resembles that of the diammine, and is not like the hexammine. F. Ephraim and co-workers studied the mol. vol. of the amines. F. W. Bergstrom observed that an ammonia soln. of **potassium amide** produces no definite products with ferrous bromide. V. Thomas, and W. Manchot found that both aq. and alcoholic soln. of ferrous bromide absorb **nitric oxide** until the solute corresponds with **ferrous nitrosyl bromide**,  $\text{FeBr}_2 \cdot \text{NO}$ , although that salt has not been isolated. V. Thomas also found that the dry, anhydrous salt absorbs **nitrogen peroxide** to form **ferrous tetrinitroxylbromide**,  $4\text{FeBr}_2 \cdot \text{NO}_2$ , which retains the absorbed gas even in vacuo. If moisture be present, more gas is absorbed, but a reaction sets in which is attended by the evolution of bromine. H. Grossmann and F. Hünseler observed that **phenylhydrazine** forms the complex  $\text{FeBr}_2 \cdot 6(\text{C}_6\text{H}_5)\text{NH}(\text{NH}_2)$ .

W. Hieber and co-workers, H. Hock and H. Stühlmann, and W. Mittasch observed that **iron carbonyl**,  $\text{Fe}(\text{CO})_5$ , in pentane or other solvent reacts with bromine forming **ferrous tetracarbonyl bromide**,  $\text{Fe}(\text{CO})_4\text{Br}_2$ . The mol. wt. in ethylene bromide is 330.7; in nitrobenzene, 339.7; and in acetic acid, 323.3—the theoretical value is 327.68. The heat of formation is  $(\text{FeBr}_2, 4\text{CO}) = 26$  Cals. The bromide decomposes in sunlight; and at press. below 750 mm., or at temp. above  $55^\circ$ , into ferrous bromide and carbon monoxide. It is fairly stable in dry air but is decomposed by water into carbon monoxide and ferrous bromide; with ammonia it forms ferrous hexamminobromide; and with pyridine,  $\text{FeBr}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$ , and  $\text{FeBr}_2 \cdot 4\text{C}_5\text{H}_5\text{N}$ . It is decomposed by ethyl acetate or acetic anhydride. If bromine acts on the iron pentacarbonyl at a low temp., **ferrous pentacarbonyl bromide**,  $\text{Fe}(\text{CO})_5\text{Br}_2$ , is formed; the complex **ferrous hemi-heptacarbonyl bromide**,  $\text{Fe}_2(\text{CO})_7\text{Br}_4$ , was also prepared. C. Chojnacky, and W. Manchot and J. Haas studied the compound formed by ferrous bromide with **ethylene**, namely, **ferrous ethylenebromide**,  $\text{FeBr}_2 \cdot \text{C}_2\text{H}_4 \cdot 2\text{H}_2\text{O}$ ; and C. Chojnacky observed that ferrous bromide also forms a compound with **acetylene**. F. Oberhauser and J. Schormüller observed that ferrous bromide forms a compound with **cyanogen**, and also with **cyanogen bromide**, namely,  $\text{FeBr}_2 \cdot \text{BrCy}$ . V. Thomas said that soln. of ferrous bromide in **ethyl alcohol** yield well-formed crystals; and similarly with soln. in ether; both soln. absorb nitric oxide. Ferrous bromide is also slightly soluble in **acetic acid**; in **ethylene chloride**; and in **benzene**; but **phenol** in the cold does not attack the salt, although when warmed the salt is blackened. A. Schier, and A. Naumann and A. Schier found that ferrous bromide forms a colourless soln. with **acetonitrile**. W. Biltz and G. F. Hüttig, and F. Ephraim and R. Linn observed that ferrous bromide unites with **methylamine** forming  $\text{FeBr}_2 \cdot 6(\text{CH}_3)\text{NH}_2$ . R. E. Breuill prepared a complex with **ethylene-diamine**,  $[\text{Fe en}_3]\text{Br}_2$ . W. Hieber and co-workers studied these compounds. According to R. Müller, 100 c.c. of **pyridine** dissolve 0.49 gm. of ferrous bromide at  $25^\circ$ , and the complex salts with  $\text{FeBr}_2 : \text{C}_5\text{H}_5\text{N} : \text{H}_2\text{O} = 1 : 5 : 0, 1 : 5 : 1, 1 : 4 : 0, 1 : 2 : 0$ , and  $1 : 2 : 2$  were studied by G. Spacu, R. Weinland and co-workers, and W. Hieber and co-workers. F. Blau, and A. Werner investigated the complex salt with ***aa'*-dipyridyl**,  $[\text{Fe}(\text{C}_{10}\text{H}_8\text{N}_2)_3]\text{Br}_2 \cdot 6\text{H}_2\text{O}$ , which L. A. Welo found to be diamagnetic. A. Werner found the complex  $[\text{Fe}(\text{Dipyr})_3]\text{Br}_2 \cdot 6\text{H}_2\text{O}$ , to be optically active. F. Blau investigated the complex salt with ***aa'*-phenanthroline**, and H. Freundlich and V. Birstein measured its mol. conductivity. L. Meyer and A. Scheufelen found ferrous bromide a useful catalyst in the bromination of organic compounds.

J. W. Retgers observed that no **ammonium ferrous bromide** is formed from an aq. soln. of the component salts; ferrous bromide has no influence on the crystalline form of ammonium bromide. P. A. von Bonsdorff prepared **mercuric ferric bromide**,  $\text{HgBr}_2 \cdot \text{FeBr}_2 \cdot 4\text{H}_2\text{O}$ , by crystallization from a soln. of the two salts. J. Kendall and co-workers obtained evidence of the formation of an **aluminium ferrous bromide**. B. Rayman and K. Preis observed that a complex

**stannic ferrous bromide** is formed from a mixed soln. of stannic and ferrous bromides.

**The preparation of ferric bromide.**—C. Löwig, and J. von Liebig prepared **ferric bromide**,  $\text{FeBr}_3$ , by heating the residue obtained by evaporating the aq. soln.—say, a soln. of iron in an excess of bromine water—the salt collects as a sublimate. P. Höfer also obtained a sublimate of brown crystals of ferric bromide by heating ferrous bromide to  $400^\circ$  to  $500^\circ$  in the absence of air. C. Löwig prepared ferric bromide by heating ferrous bromide with bromine; and A. Scheufelen recommended heating the mixture of ferrous bromide with twice its weight of bromine in a sealed tube at  $170^\circ$  to  $200^\circ$ . F. Ephraim and S. Millmann obtained the salt by exposing powdered iron for many months to the vapour of bromine in a desiccator. C. L. Jackson and I. H. Derby observed that anhydrous ferric bromide is formed when bromine vapour acts on ferrous hexamminiodide. M. Barre obtained ferric bromide by passing the vapour of sulphur monobromide over ferric oxide at  $450^\circ$  to  $650^\circ$ . The reaction begins at  $300^\circ$ . O. Hönigschmid and co-workers discussed the preparation, and J. C. Hostetter and H. S. Roberts, the purification of the salt.

**The hydrates of ferric bromide.**—According to A. J. Balard, whilst bromine water converts hydrated ferrous oxide into hydrated ferric oxide and ferrous bromide, not a trace of ferric oxide is taken up. C. Löwig, A. E. Schaefer, J. Nicklès, A. Christensen, H. Lescœur, and L. L. de Koninck found that a soln. of ferric bromide is obtained by dissolving the anhydrous salt in water, by dissolving hydrated ferric oxide in hydrobromic acid, or by adding bromine water to a soln. of ferrous bromide. If the soln. is to contain  $\text{Fe} : \text{Br} = 1 : 3$ , it must not be warmed or else bromine will be evolved. The yellowish-brown soln. is darker in colour than the soln. of the corresponding chloride; it has a ferruginous taste; it gives off hydrogen bromide when evaporated, and deposits an oxybromide; it does not yield crystals when evaporated to a syrupy consistency; but when evaporated to dryness, it yields a mixture of ferric oxybromide and bromide—the latter can be separated by sublimation. According to I. Bolschakoff, if the dark brown aq. soln. be concentrated in a desiccator over sulphuric acid, it deposits the *hexahydrate*,  $\text{FeBr}_3 \cdot 6\text{H}_2\text{O}$ , in spherical clusters of small, dark green needles isomorphous with the corresponding hexahydrated chloride. H. Lescœur inferred from his vap. press. measurements that there are two other hydrates: *trihydrate*,  $\text{FeBr}_3 \cdot 3\text{H}_2\text{O}$ , and *hemitrihydrate*,  $\text{FeBr}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ .

**The physical properties of ferric bromide.**—C. Löwig described the anhydrous salt as a dark red, crystalline mass; and A. Scheufelen added that **crystals** of the sublimed salt furnish six-sided, rhombic plates with a metallic lustre. The salt is very deliquescent. A. Bromer gave 1.0107 for the **specific gravity** of an aq. soln. with 1.56 per cent.  $\text{FeBr}_3$ , and 1.0641 for a soln. with 8.016 per cent. A. Scheufelen observed that ferric bromide cannot be sublimed by heat without some decomposition; and when heated in an evacuated tube, it dissociates into ferrous bromide and bromine, but ferric bromide is re-formed on cooling. The subject was discussed by G. P. Baxter, and O. Hönigschmid and co-workers. I. Bolschakoff observed that the **melting-point** of the hexahydrate is  $27^\circ$ , and melting occurs without decomposition. J. Nicklès, L. L. de Koninck, and I. Bolschakoff also observed that at its **boiling-point**, the aq. soln. dissociates into ferrous bromide and bromine. H. Lescœur found the **vapour pressure** of the trihydrate at  $40^\circ$  is about 11.9 mm., and of the hemitrihydrate, 5.5 mm. According to T. Andrews, the thermal value of the reaction  $2\text{FeBr}_3 \cdot \text{Aq} + \text{Fe} = 3\text{FeBr}_2 \cdot \text{Aq} + 48.9$  Cals.; and since  $(\text{Fe}, \text{Br}_2, \text{Aq}) = 80.8$  Cals., the **heat of formation** is  $(2\text{FeBr}_2, \text{Br}_2, \text{Aq}) = 31.9$  Cals. J. Thomsen made observations on this subject. M. Berthelot gave  $(2\text{Fe}, 3\text{Br}_{2\text{liq}}) = 190.9$  Cals. and  $(2\text{Fe}, 3\text{Br}_{2\text{gas}}, \text{Aq}) = 212.1$  Cals.; and for the **heat of neutralization**,  $[\text{Fe}_2\text{O}_{3\text{ppd}}, 6\text{HBr}] = 33.2$  Cals. A. Scheufelen noted that heat is evolved when the anhydrous salt is dissolved in water; and T. Andrews studied the **heat of solution** of the salt.

A. Bromer gave for the **index of refraction** of aq. soln. :

	1.56 per cent. $\text{FeBr}_3$ (19°)			8.016 per cent. $\text{FeBr}_3$ (20°)	
	C-line	D-line	F-line	C-line	D-line
$\mu$ . . . .	1.33373	1.33575	1.33698	1.34518	1.34748

The **molecular refraction** of the first soln. with the  $\mu^2$ -formula is 76.11 ; and of the second soln., 81.07. The colour of aq. soln. of ferric bromide changes with dilution like the soln. of ferric chloride. Dil. soln. are yellow, and conc. soln. are dark brown, almost black. S. U. Pickering found that soln. with 1.0 to 0.1 grm. Fe per litre change their colour on standing until the hydrolysis has attained a stable end-state. J. S. Anderson found the **molecular extinction**,  $k$ , of soln. with  $C$  mols of  $\text{FeBr}_3$  per litre, to be :

$\lambda$ . . . .	4,340	4,860	5,470	6,020	6,770	7,100	7,880	10,620	13,000 A.
$k$ { $C=2.0$ . . . .	—	—	—	—	3.00	1.95	1.4	2.4	0.95
$C=1.0$ . . . .	—	—	—	2.74	0.87	0.85	0.88	1.19	0.61
$C=0.2$ . . . .	57.5	17.0	2.0	0.37	0.21	0.24	0.36	0.56	0.32

The effects of hydrolysis are not here apparent, but with soln. of conc. between 0.2 and 0.02 mol  $\text{FeBr}_3$  per litre, the effects of hydrolysis appear. Thus, with fresh soln., and soln. six weeks old :

	$\lambda = 6530 \text{ A.}$				$\lambda = 4530 \text{ A.}$	
$C$ . . . .	2.0	1.4	0.8	0.2	0.2	0.02
$k$ { Fresh . . . .	5.9	1.26	0.33	0.19	31.7	11.3
Aged . . . .	4.0	0.96	0.28	0.17	29.0	27.4

Unlike soln. of ferric nitrate and sulphate,  $k$  here decreases with decreasing concentration. There is an absorption band in the ultra-red which with increasing concentration moves towards the violet. The absorption is more intense than it is with soln. of other ferric salts, and it is possible that this is due to the separation of some free bromine. This subject was discussed by R. A. Houstoun and co-workers.

N. Sasaki's observations on the **electrical conductivity** of soln. of mixtures of ferric chloride with potassium chloride and bromide indicated that the **degree of ionization** of ferric bromide is nearly the same as that of the other halides. R. Peters' observations on electrode potentials indicate that the bromide is less ionized than is the case with the chloride. R. Peters inferred that the hydrolysis of ferric bromide is greater than is that of the chloride. W. Isbekoff gave 0.92 volt for the decomposition potential of ferric bromide dissolved in molten zinc bromide. L. Riéty studied the potential difference between soln. of ferric chloride and the glass walls of a capillary containing the liquid. O. Liebknecht and A. P. Wills gave  $50 \times 10^{-6}$  unit for the **magnetic susceptibility** of a feebly acidic soln. of ferric chloride at 18°. A. Quartaroli said that with a feebly acidic soln. having 2.88 grms. of  $\text{FeBr}_3$  per litre, the paramagnetism of the solute, and the diamagnetism of the solvent almost neutralize one another. Observations were also made by B. Cabrera and E. Moles.

**Chemical properties of ferric bromide.**—According to H. Schulze, when the vapour of ferric bromide and **oxygen** is heated to redness, ferric oxide and bromine are formed. The **hydrolysis** of a soln. of ferric bromide in **water** has just been indicated, and C. Löwig reported that a **ferric oxybromide** is formed as a residue on evaporating an aq. soln. of the salt to dryness. A. Béchamp reported an oxybromide,  $\text{FeBr}_3 \cdot 7\text{Fe}_2\text{O}_3$ , to be formed as a deep red soln. by leaving hydrated ferric oxide in contact with an aq. soln. of ferric bromide for three months, and  $\text{FeBr}_3 \cdot 5\text{Fe}_2\text{O}_3$  to be formed by the action of silver nitrate on a soln. of ferric bromide. J. M. Ordway said that hydrobromic acid dissolves at least 5 equivalents of ferric oxide, and A. Béchamp observed that a soln. of ferric bromide dissolves hydrated ferric oxide as readily as does a soln. of ferric chloride ; and C. Löwig added that a soln. of ferric bromide can dissolve at least 5 eq. of hydrated

ferric oxide. The peptization of hydrated ferric oxide by soln. of ferric bromide was also discussed by S. U. Pickering, P. Nicolardot, and A. W. Thomas and E. R. Hamburger—*vide supra*, the hydrosols and hydrogels of ferric oxide. There is here no definite evidence of the existence of an oxybromide as a chemical individual. A. Scheufelen, and E. Beckmann observed that ferric bromide is slightly soluble in **bromine**. E. C. Franklin and C. A. Kraus found that ferric bromide is slightly soluble in liquid **ammonia**; H. Hunt and L. Boneyk said that it is insoluble in liquid ammonia at 25°; and F. Ephraim and S. Millmann said that the anhydrous salt in ammonia swells up to three times its vol. forming **ferric hexamminobromide**,  $\text{FeBr}_3 \cdot 6\text{NH}_3$ , whose dissociation press.,  $p$  mm., is:

	0°	16°	30.5°	40.2°	49°	53°
$p$	73	156	331	490	661	734

and the heat of dissociation is 11.2 Cals. per mol. of ammonia. V. Thomas found that **nitric oxide** is not absorbed by the anhydrous salt at ordinary temp., and when heated, the salt is reduced:  $\text{FeBr}_3 + \text{NO} = \text{NOBr} + \text{FeBr}_2$ ; no complex with **nitrogen peroxide** is formed at ordinary temp., and at 300°, ferric oxide is formed.

A. Scheufelen found that ferric bromide is soluble in **alcohol** and **ether**; and I. Bolschakoff obtained a similar result with the hexahydrate. A. Rosenheim and P. Müller found that the salt is soluble in **acetic acid**; and G. Grünberg-Krasnowskaja studied the complex bromoacetates. A. Scheufelen investigated the action of ferric bromide on **nitrobenzene** and **nitrotoluene**; A. Schier, and A. Naumann and A. Schier showed that ferric bromide forms a blood-red soln. with **acetonitrile**; and G. Spacu, that it is reduced by **pyridine** to ferrous bromide, and it also forms a complex salt  $\text{Fe}(\text{OH})\text{Br}_2 \cdot \text{C}_5\text{H}_5\text{N}$ . W. Hieber and co-workers studied the pyridine compounds as well as those of **ethylenediamine**, and of **carbon monoxide**. G. A. Barbieri observed that ferric bromide forms a complex with **urea**; F. Calzolari, a complex with **antipyrine**; F. Oberhauser and J. Schormüller, with **cyanogen bromide**; P. Pistschimuka, with **methyl thiophosphate**; A. Bayer and H. Aickelin, with **tri-p-chlorotriphenyl-carbinol bromide**; and R. Fosse and L. Lesage, with **xanthylum bromide**. L. Meyer and A. Scheufelen, and L. Bruner and J. Fischler found that ferric bromide is a useful catalyst in the bromination of organic compounds.

J. Nicklès found that an aq. soln. of ferric bromide, at the temp. of a water-bath, or when exposed to sunlight, slowly dissolves **gold**, even when no excess of bromine is present. W. Isbekoff found that molten **zinc bromide** dissolves 11.57 per cent. of ferric bromide; and B. A. Isbekoff and W. A. Plotnikoff, that **aluminium bromide** forms a dark red soln. with ferric bromide, and the sp. conductivity of a 20 per cent. soln. is 0.001 mho at 150°. J. Nicklès observed that the tendency of the ferric halides to form complex salts increases with the at. wt. of the halogen. A few complex salts have been prepared. J. W. Retgers observed that no solid soln. is formed between ferric and ammonium bromides; and C. Löwig noted that if in aq. soln. a complex is formed with ammonium bromide it is readily dissociated on crystallization. P. T. Walden obtained **ammonium ferric tetrabromide**, or *ammonium tetrabromoferrate*,  $\text{NH}_4\text{FeBr}_4 \cdot 2\text{H}_2\text{O}$ , in deliquescent, dark green crystals, from a soln. of one part of ammonium bromide to five of ferric chloride. There is some uncertainty about the proportion of water of crystallization. The salt decomposes when it is re-crystallized from its aq. soln. No success was obtained in the attempt to prepare  $(\text{NH}_4)_2\text{FeBr}_5$ . When a soln. containing  $\text{NH}_4\text{Br} : \text{FeBr}_3 = 2 : 1$  is crystallized, both the tetrabromoferrate and ammonium bromide crystallize from the same soln. No **potassium ferric bromide** could be prepared by C. Löwig. F. Krauss and T. von Heidelberg obtained complex salts of rubidium and caesium bromides. By crystallizing a soln. containing 5 grms. of rubidium bromide and 6 grms. of ferric bromide, P. T. Walden obtained dark green, short, doubly terminated prisms of rubidium ferric pentabromide, or **rubidium pentabromoferrate**,  $\text{Rb}_2\text{FeBr}_5 \cdot \text{H}_2\text{O}$ . The salt is rapidly decomposed in air, and

on re-crystallization from its aq. soln. The analogous **cæsium ferric pentabromide**, or *cæsium pentabromoferrate*,  $\text{Cs}_2\text{FeBr}_5 \cdot \text{H}_2\text{O}$ , was obtained from a soln. of equal proportions by weight of the component salts. It resembles the rubidium salt but it is comparatively stable. A soln. of cæsium bromide with twice its weight of ferric bromide furnishes dark green, slender needles of **cæsium ferric tetrabromide**, or *cæsium tetrabromoferrate*,  $\text{CsFeBr}_4$ . No **sodium ferric bromide** was prepared by C. Löwig. R. F. Weinland and H. Schmid prepared **antimony ferric octodecachloride**,  $\text{Fe}(\text{SbBr}_6)_3$ , or  $\text{FeBr}_3 \cdot 3\text{SbBr}_5$ .

According to C. Lenormand, bromine acts very slowly on anhydrous ferrous chloride at the ordinary temp., combination being incomplete even after a month. In sealed tubes at about  $100^\circ$ , the result varies with the proportion of bromine employed. If the chloride and the bromine are mixed in the proportions  $2\text{FeCl}_2 : \text{Br}_2$ , combination takes place, but no crystals are formed; if, however, the bromine is in excess, **ferric dichlorobromide**,  $\text{FeCl}_2\text{Br}$ , separates in volatile crystals which are insoluble in an excess of bromine. Again, when bromine is added to ferrous chloride soln., combination takes place with development of considerable heat, and, after expulsion of the excess of bromine, the composition of the liquid agrees with the formula  $\text{FeCl}_2\text{Br}$ . The soln. is very deep red when concentrated, and yellow when dilute. It has an acidic reaction, and contains colloidal ferric oxide. It separates in volatile crystals which are insoluble in excess of bromine. The crystals are lustrous, and very dark coloured, green by reflected light, and completely opaque even in thin sections. They seem to be hexagonal tables. The compound is very deliquescent, and very soluble in water; it also dissolves readily in alcohol or ether, and, by means of the latter, can be separated from ferrous chloride. Chloroform, benzene, and toluene also dissolve it, but carbon bisulphide dissolves only a trace. It is easily decomposed by heating, but sublimes readily when heated in a tube containing a slight excess of bromine.

F. Krauss and T. von Heidelberg prepared a series of mixed salts by the action of ferric chloride or bromide on various alkali hydrides in soln. acidified strongly with the corresponding halogen acid. In this way, they prepared **rubidium ferric dichlorotribromide**,  $\text{Rb}_2[\text{FeBr}_3\text{Cl}_2(\text{H}_2\text{O})]$ ; **rubidium ferric trichlorodibromide**,  $\text{Rb}_2[\text{FeCl}_3\text{Br}_2(\text{H}_2\text{O})]$ ; **cæsium ferric dichlorotribromide**,  $\text{Cs}_2[\text{FeBr}_3\text{Cl}_2(\text{H}_2\text{O})]$ ; **cæsium ferric trichlorodibromide**,  $\text{Cs}_2[\text{FeBr}_2\text{Cl}_3(\text{H}_2\text{O})]$ ; **triethylammonium ferric chlorotribromide**,  $\text{HN}(\text{C}_2\text{H}_5)_3[\text{FeClBr}_3]$ , melting at  $39.5^\circ$  with decomposition; **triethylammonium ferric trichlorobromide**,  $\text{HN}(\text{C}_2\text{H}_5)_3[\text{FeCl}_3\text{Br}]$ ; and **pyridinium trichlorobromide**,  $\text{C}_5\text{H}_5\text{NH}[\text{FeCl}_3\text{Br}]$ , melting at  $84^\circ$ . E. A. Dancaister studied the formation of **ferric trichlorohexabromide**,  $\text{FeCl}_3\text{Br}_6$ , in non-aqueous soln.

F. Oberhauser and J. Schormüller treated ferrous bromide for a long time with an excess of cyanogen bromide and obtained a complex  $\text{Fe}_3\text{Br}_8\text{Cy}_2 \cdot 3\text{CyBr}$ ; when this salt is heated between  $160^\circ$  and  $200^\circ$ , it forms **ferrosic bromide**,  $\text{Fe}_3\text{Br}_8$ , with a dissociation press. of 12 mm. at  $100^\circ$ . The complex is formulated on A. Werner's co-ordination scheme,  $\text{Fe}''[\text{Fe}'''\text{Br}_4]_2$ , and the hexahydrate,  $[\text{Fe}''(\text{H}_2\text{O})_6][\text{Fe}'''\text{Br}_4]_2$ . H. Chandra obtained yellow, trigonal crystals of the *decahydrate*,  $\text{Fe}_3\text{Br}_8 \cdot 10\text{H}_2\text{O}$ , by dissolving hydrated ferrosic oxide in well-cooled, saturated hydrobromic acid, and evaporating the soln. below  $5^\circ$ , over sulphuric acid and lime. The *hexahydrate*,  $\text{Fe}_3\text{Br}_8 \cdot 6\text{H}_2\text{O}$ , was prepared by A. Höhn, and R. Weinland and co-workers—A. Höhn, and H. Holtmeier—in dark red, deliquescent crystals, by dissolving hydrated ferric oxide in the theoretical quantity of hydrobromic acid, and evaporating the soln. on a water-bath. The salt is blackened in light. If sodium acetate be added to the dark red soln. of ferrosic bromide, a complex ferrosic acetate is precipitated. R. Weinland with H. Holtmeier, and with A. Höhn, prepared complex salts in which the ferrous salt was replaced by salts—acetates, propionates, benzoates, etc.—of other bivalent metals—nickel, cobalt, manganese, magnesium, zinc, and cadmium. F. Oberhauser and J. Schormüller prepared complexes with cyanogen bromide,  $\text{Fe}_3\text{Br}_8 \cdot 4\text{CyBr}$ ; with hydrogen cyanide,  $\text{Fe}_3\text{Br}_8 \cdot 5\text{HCy}$ ; and with cyanogen,  $\text{Fe}_3\text{Br}_8 \cdot n\text{Cy}_2$ .



P. T. Walden found that when the attempt was made to prepare a complex of potassium and ferric bromides, from a soln. of potassium bromide with five times its weight of ferric bromide, a green salt, **potassium ferrosic bromide**,  $\text{KBr} \cdot \text{FeBr}_2 \cdot 2\text{FeBr}_3 \cdot 3\text{H}_2\text{O}$ , separated out in dark green, opaque, cubic crystals which gave a black hydroxide when treated with ammonia. The analogous **rubidium ferrosic bromide**,  $\text{RbBr} \cdot \text{FeBr}_2 \cdot 2\text{FeBr}_3 \cdot 3\text{H}_2\text{O}$ , separated in dark green, opaque, rhombohedral crystals from a soln. of rubidium bromide with five times its weight of ferric bromide. Ammonium, and the other alkalies did not form an analogous salt.

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### § 39. The Iron Iodides

J. L. Gay Lussac,<sup>1</sup> and H. Davy noted that iodine readily unites with iron, with a slight evolution of heat, forming a brown mass which fuses at a red-heat and volatilizes at a higher temp. J. D. Smith first analyzed and established the individuality of **ferrous iodide**, FeI<sub>2</sub>. G. S. Sérullas prepared the anhydrous salt by passing the vapour of iodine and steam through a red-hot iron tube filled with charcoal. In 1861, L. Carius and J. A. Wanklyn prepared ferrous iodide by rapidly heating to redness iron turnings in a covered porcelain crucible, and frequently adding small quantities of iodine. The iron was initially mixed with a little iodine to drive out the air. The excess of iodine is volatilized. As the temp. falls below redness, there is suddenly developed a quantity of iodine vapour. This phenomenon may mean that ferric iodide is stable above the critical temp. or that iodine is occluded by fused ferrous iodide in a way analogous to the absorption of oxygen by fused silver. L. Carius and J. A. Wanklyn's product was a grey, laminated mass, but C. L. Jackson and I. H. Derby have shown the product is obtained in the form of red scales if air be excluded; the grey colour is an effect produced by the absorption of moisture from the air; and they prepared the salt by passing hydrogen and iodine vapour over heated ferric oxide; and by heating clippings of iron wire in a steel bicycle tube to a bright red-heat, and passing the vapour of iodine in a stream of nitrogen through the tube. Iron wire clippings gave better results than iron turnings or fillings, or reduced iron. A smaller steel bicycle tube was slipped into the exit end of the heated tube; and the ferrous iodide, volatilized from the larger tube, condensed in the smaller tube from which it was easily removed. The exit tube from the condensing tube passed through sulphuric acid, and the iodine which collected was used again. In order to avoid the loss of iodine, M. Guichard recommended using a tube containing iron and iodine, separated by an asbestos plug. The tube was evacuated, sealed, and heated in such a manner that the iron was kept at 500°, and the iodine at 180°. Ferrous iodide is formed, and it sublimes in the form of deep red crystals. It was prepared by M. Berthelot,

W. Biltz and G. F. Hüttig, B. Köhnlein, and A. E. Nordenskjöld, from iron and hydrogen iodide, or iodine and hydrogen; by C. L. Jackson and I. H. Derby, from ferrous oxide, iodine and hydrogen; and by W. Biltz and G. F. Hüttig, C. L. Jackson and I. H. Derby, H. Lesceur, and A. T. Thomson, by dehydrating the hydrated salt. E. Filhol and J. Melliès obtained it by the action of iodine on one of the iron sulphides at 200°; L. Hackspill and R. Grandadam, by heating a mixture of iron and sodium iodide:  $\text{Fe} + 2\text{NaI} = \text{FeI}_2 + 2\text{Na}$ ; and by W. Hieber and G. Bader, by the photochemical decomposition of ferrous tetracarbonyl iodide. Its formation in blowpipe testing was discussed by P. Casamajor, and J. Landauer. According to C. L. Jackson and I. H. Derby, the salt can be purified by sublimation in an atmosphere of nitrogen, carbon dioxide, or hydrogen provided oxygen is excluded.

**The hydrates of ferrous iodide.**—In 1842, A. T. Thomson treated iron with twice its weight of iodine suspended in water, and after evaporating off the water in the presence of metallic iron contained in a flask, obtained a steel-grey, laminated mass of ferrous iodide. G. M. Beringer, M. Berthelot, F. Chemnitz, A. Dupasquier, E. Fleury, M. Kop, J. H. Long, J. D. Smith, A. T. Thomson, and F. A. Volkmann studied the subject. A soln. of ferrous iodide is obtained by digesting, in the presence of water, iron filings with three to four times its weight of iodine. J. L. Gay Lussac, C. L. Jackson and I. H. Derby, and W. Biltz and E. Birk obtained the aq. soln. by dissolving anhydrous ferrous iodide in water; much heat is evolved. Dil. soln. are colourless, and conc. soln. are green.

Hydrates of ferrous iodide of indefinite composition were reported by A. Dupasquier, G. Kerner, A. P. J. du Mênil, L. Miahle, J. Preuss, and J. D. Smith. When a red crystal of ferrous iodide is exposed to air, a white border first appears and the whole crystal becomes white; this change is soon followed by the liberation of iodine which imparts a grey or black appearance. The change from red to white is an effect of moisture, it does not occur when the iodide is confined in a dry, inert medium—e.g., carbon dioxide, dry ether, etc.—but it does occur if moisture be present. C. L. Jackson and I. H. Derby found the white product had a composition corresponding with the *dihydrate*,  $\text{FeI}_2 \cdot 2\text{H}_2\text{O}$ . H. Lesceur's measurements of the vap. press.,  $p$ , of the dihydrate indicated that at 90°,  $p$  falls from 77 mm. to 20 mm. as the dihydrate passes to the monohydrate,  $\text{FeI}_2 \cdot \text{H}_2\text{O}$ ; and at 160°, the monohydrate gradually forms the anhydrous salt. A hot, sat. soln. of ferrous iodide deposits green crystals of the *tetrahydrate*,  $\text{FeI}_2 \cdot 4\text{H}_2\text{O}$ , on cooling. According to G. Kerner, a boiling soln. deposits dark green, rhombic plates of the *pentahydrate*,  $\text{FeI}_2 \cdot 5\text{H}_2\text{O}$ , and sp. gr. 2.873. J. D. Smith obtained similar crystals by evaporating a soln. on the water-bath. F. A. Volkmann, however, showed that the crystals obtained by evaporating aq. soln. of ferrous iodide are the tetrahydrate,  $\text{FeI}_2 \cdot 4\text{H}_2\text{O}$ . These crystals melt in their water of crystallization between 90° and 98°; have a sp. gr. of 2.873 at 12°; and, according to J. D. Smith, when heated in air they give off water and iodine, and leave ferric oxide; they blacken when heated to 50°, but the original colour is restored on cooling. F. A. Volkmann, and H. Lesceur prepared pale yellow, needle-like crystals of the *hexahydrate*,  $\text{FeI}_2 \cdot 6\text{H}_2\text{O}$ , by cooling a soln.  $\text{FeI}_2 + 8.5\text{H}_2\text{O}$  to  $-16^\circ$ , or by seeding a slowly cooled soln. with a crystal of the hexahydrate. The hexahydrate fuses at 8° and decomposes into the tetrahydrate. F. A. Volkmann obtained green plates of  $\text{FeI}_2 \cdot 9\text{H}_2\text{O}$ , by cooling the mother-liquor from the preceding hydrate to  $-11^\circ$ ; by seeding a soln.  $\text{FeI}_2 + 10.5\text{H}_2\text{O}$  cooled to  $-10^\circ$  with a fragment of the solid obtained by cooling a soln.  $\text{FeI}_2 + 9\text{H}_2\text{O}$  to  $-30^\circ$ . This salt is less deliquescent than the hydrates just considered; it melts between 0° and 2.5°.

**The physical properties of ferrous iodide.**—J. L. Gay Lussac, H. Davy, B. Köhnlein, and M. Guichard said that anhydrous ferrous iodide, when sublimed, forms plate-like crystals of a deep red colour with a brownish tint; in thicker masses the colour of ferrous iodide is nearly black. When melted and allowed to solidify, it forms a reddish-black crystalline mass with a brown tinge on the fractured surface. W. Biltz and G. F. Hüttig said that the crystals are black in

reflected, and garnet-red in transmitted light. A. Ferrari and F. Giorgi found that the crystals are of the cadmium iodide type, and the X-radiograms correspond with a unit cell with the parameters  $a=4.04$  Å., and  $c=6.75$  Å. Some of the older observers, C. L. Jackson and I. H. Derby, S. de Luca, A. E. Nordenskjöld, A. T. Thomson, and L. Carius and J. A. Wanklyn, said that the powder is grey or white. This, as indicated above, was shown by A. E. Nordenskjöld, and C. L. Jackson and I. H. Derby to be due to the formation of the grey dihydrate on exposure to air, and these same observers said that the crystals are six-sided plates belonging to the hexagonal system, and they are optically uni-axial. The general appearance of the crystals of the hydrates is indicated above. G. S. Sérullas' description of his product as "shining yellow crystals resembling gold filings," has not been confirmed, although ferrous bromide has a dark yellow colour with a greenish-brown tinge. W. Biltz and E. Birk gave 5.315 for the sp. gr. of the sublimed salt at  $25^{\circ}/4^{\circ}$ . W. Biltz said that the mol. vol. is 58.27 at  $25^{\circ}$ , and he showed that the formation of the compound from its elements is attended by an expansion. J. L. M. Poiseuille studied the rate of flow of the soln. in a capillary tube. R. Hanslian measured the lowering of the b.p. of iodine by the dissolution of iron. H. Lesceur found the vap. press.,  $p$  mm., of the sat. soln.:

	$50^{\circ}$	$60^{\circ}$	$70^{\circ}$	$80^{\circ}$	$90^{\circ}$
$p$ . . . . .	30	50	74	101	144

and for the dihydrate,  $p=77, 115, 160$ , and  $233$  mm. respectively at  $90^{\circ}, 100^{\circ}, 110^{\circ}$ , and  $120^{\circ}$ ; and for the monohydrate,  $110$  mm. at  $160^{\circ}$ . F. Ephraim and co-workers also studied the mol. vol. H. Davy, and J. L. Gay Lussac observed that the anhydrous salt melts at a red-heat. According to A. T. Thomson, the anhydrous salt melts at  $177^{\circ}$ . A. Ferrari discussed the relation between the m.p. and the space-lattice. H. Davy observed that the anhydrous salt is volatile at a high temp.; and C. L. Jackson and I. H. Derby showed that it sublimes when heated in a stream of inert gas—nitrogen, carbon dioxide, or even hydrogen—oxygen must be rigorously excluded. According to T. Andrews, the heat of formation in soln. is  $(\text{Fe}, \text{I}_2, \text{Aq.})=46.4$  Cals.; J. Thomsen gave  $47.65$  Cals.; and M. Berthelot,  $47.7$  Cals., and  $(2\text{Fe}, \text{I}_{2\text{gas}}, \text{Aq.})=61.3$  Cals. J. Thomsen gave  $(\text{Fe}, 2\text{HI}, \text{Aq.})=21.34$  Cals. Observations were also made by P. A. Favre and J. T. Silbermann. G. Beck studied the free energy of the salt; and F. Ephraim and O. Schütz, the relation between the heat of formation and the mol. vol. A. Mosnier found that the heat of soln. of the anhydrous salt in 73 parts of water is  $23.3$  Cals. G. Beck, and W. Herz calculated values for the entropy and vibration frequency of  $\text{FeI}_2$ ; and E. Rabinowitsch and E. Thilo studied the heat of formation. W. Hieber and A. Woerner gave  $(\text{Fe}, \text{I}_2)=30.12$  Cals.; and W. Hieber and E. Levy studied the lattice energy of the crystals.

A. K. Chapman studied the emission spectrum of anhydrous ferric iodide, and also of the aq. soln. D. J. P. Berridge obtained photographic prints with paper saturated with ferrous iodide, but the sensitivity was less than with other soluble iodides. M. Padoa and N. Vita found that under the influence of pulsating radiations of wave-lengths  $670.8, 587$  to  $589.6, 535$ , and  $460.7$  Å., corresponding with quanta of  $42.51, 48.57$  to  $48.35, 53.30$ , and  $61.9$  cal. respectively, the reaction  $2\text{FeI}_2 + \text{I}_2 \rightarrow 2\text{FeI}_3$  gave the following relative maximal yields:  $1.40, 1.60, 1.70$ , and  $2.15$ . This shows that the greater the light quanta, the higher the yield. A minimum of  $30$  cal. is necessary to start the reaction, and the yields are then proportional to the quanta. The curves showing the relation between the yields with intermittent or continuous light indicate frequent periodic oscillations for light of short wave-length, and similar periods of somewhat less frequency for light of longer wave-length. The oscillations are explained by assuming the existence of active mols. which are the seat of adiabatic transformations and the period of existence of which appears to be the longer, the higher are their energy levels. N. Sasaki and K. Nakamura measured the potential of mixed soln. of  $\text{Fe}^{++}/\text{Fe}^{+++}$

and of  $I/I'$ , and found it to be influenced solely by the concentration of the iodide and free iodine. They also studied the Becquerel effect with these soln. M. Faraday found that the anhydrous salt is paramagnetic. O. Liebknecht and A. P. Wills gave  $42 \times 10^{-6}$  mass unit for the magnetic susceptibility of a soln. of ferrous iodide at  $18^\circ$ . L. Pauling and M. L. Huggins studied the magnetic properties. A. Schükareff observed a magnetochemical effect when, in the electrolysis of a soln. of ferrous iodide, the anode is in a magnetic field.

**The chemical properties of ferrous iodide.**—According to C. L. Jackson and I. H. Derby, ferrous iodide can be sublimed in an atm. of **hydrogen** without change, and the result is similar when hydrogen is passed through molten ferrous iodide, or when a mixture of hydrogen and ferrous iodide vapour is passed over iron. Hydrogen can also be bubbled through an aq. soln. of ferrous iodide without a reduction of the salt. According to H. Schulze, and C. L. Jackson and I. H. Derby, anhydrous ferrous iodide is very susceptible to oxidation, so that when heated in **air**, even at a moderate temp., all the iodine passes off in violet fumes and a residue of ferric oxide is formed which retains the shape of the iodide crystals. B. Köhnlein said that the crystals of ferrous iodide are very deliquescent; W. Biltz and E. Birk did not find them particularly deliquescent. C. L. Jackson and I. H. Derby's observations are indicated above in connection with the dihydrate. H. Lescœur said that the salt can be preserved in dry air, but C. L. Jackson and I. H. Derby reported that the decomposition of ferrous iodide by the oxygen of the air takes place at ordinary temp., for when confined in a desiccator, it soon colours the confined atmosphere purple. This subject was discussed by A. T. Thomson, and S. de Luca. According to J. Preuss, when the powdered hydrate of ferrous iodide is kept for four months in a stoppered bottle, it becomes covered with a film of iodine, and afterwards, it is but partially soluble in **water** since it forms a dark brown soln. and leaves a residue of ferric oxide. According to A. Dupasquier, M. Kop, A. P. J. du Mênil, C. L. Jackson and I. H. Derby, and O. van Schoor, the aq. soln. is colourless or bluish-green; it oxidizes easily in air precipitating yellowish-brown hydrated ferric oxide, or a basic iodide, and liberating iodine; according to J. J. Berzelius, J. Preuss, and J. D. Smith, the soln. can be evaporated without oxidation only in an atmosphere of an inert gas—and the soln. gives with water a precipitate of hydrated ferric oxide and iodine. C. F. Schönbein studied the oxidation of the compound in the presence of mercury. F. A. Volkmann said that the oxidation of the aq. soln. is accelerated by free iodine. According to G. Kerner, and L. Miahle, when the aq. soln. is concentrated in a retort until it froths up and assumes the consistency of oil, it solidifies, on cooling, to a greenish-black, crystalline mass, which is readily oxidized. R. Phillips assumed that in the decomposition of a soln. of ferrous iodide, hydriodic acid is first formed, and the decomposition of that acid produces iodine. J. H. Long estimated from the effect of  $0.5N\text{-FeI}_2$  on the inversion of cane-sugar that the degree of hydrolysis of the aq. soln. was 0.078 per cent. According to C. Frederking, the tendency to oxidation may be almost wholly prevented by adding twice as much sugar as iodine, and evaporating the soln. to the consistency of a syrup. C. F. Möhr, G. Kerner, H. and T. Smith, and W. Onion recommended a similar process. The *liquor ferri iodidi* and *syrupus ferri iodidi* of the pharmacopœia are colourless soln. of iron wire in iodine water. In the latter case the soln. is mixed with glucose. The soln. is used only when freshly prepared on account of its tendency to change by oxidation. The preservation of the aq. soln. from oxidation by additions of sugar, honey, glycerol, hypophosphorous acid, etc., was discussed by W. C. Alpers, H. V. Vrný and co-workers, G. M. Beringer, P. Bohrisch, A. Dupasquier, M. Geiseler, H. Hager, A. Oberdörffer, R. H. Parker, and A. T. Thomson. According to P. Squire, if a coil of iron wire be placed in a soln. of ferrous iodide, hydrated ferric oxide is precipitated, but iodine is not liberated. According to C. Weltzien, the aq. soln. of ferrous iodide is decomposed by **hydrogen dioxide** with the separation of iodine and the formation of hydrated ferric oxide. C. F. Schönbein found that **ozone**

mixed with air reacts at once with the soln. forming hydrated ferric oxide and iodine. If potassium carbonate be added to a soln. containing three mols of ferrous iodide, and two of iodine, hydrated ferrous and ferric oxides are precipitated, and potassium iodide remains in soln. It has been suggested, without proof, that the original soln. contained  $\text{Fe}_3\text{I}_8$ .

According to C. L. Jackson and I. H. Derby, although so susceptible to oxidation, ferrous iodide resists the action of reducing agents to a marked degree. A soln. of ferrous iodide dissolves **iodine**—*vide infra*, ferric iodide. C. F. Schönbein found that **sulphur dioxide** added to an aq. soln. of ferrous iodide makes it yellow, and the colour disappears on heating, or on adding aq. ammonia or alkali lye. H. Davy observed that when anhydrous ferrous iodide is exposed to dry **ammonia**, the gas is absorbed, and C. L. Jackson and I. H. Derby added that between  $0^\circ$  and  $100^\circ$ , a voluminous white powder, **ferrous hexamminoiodide**,  $\text{FeI}_2 \cdot 6\text{HN}_3$ , is formed. The compound was also prepared by F. Ephraim. W. Biltz and G. F. Hüttig cooled the iodide with a mixture of alcohol and solid carbon dioxide whilst the absorption of ammonia was in progress. W. Hieber and G. Bader prepared the hexammine by passing ammonia over ferrous tetracarbonyl iodide. W. Biltz and G. F. Hüttig, and E. Weitz and H. Müller obtained the impure hexammine by the action of ammonium iodide on an ammoniacal soln. of ferrous hexamminoacetate, and by passing ammonia into a soln. of ammonium and ferrous iodides. E. Weitz and H. Müller found that the salt prepared by the wet process furnishes pale green octahedra; the product obtained by the dry process is a voluminous white powder. W. Biltz added that like the hexammines of the other ferrous halides, the crystals are cubic, with a space-lattice having the parameter  $a=10.99 \text{ \AA}$ , and the arrangement of the atoms of iron, and iodine, and the ammonia molecules is analogous to that of the hexamminochloride. G. B. Naess and O. Hassel studied the sphere of action of the anion. W. Biltz and E. Birk found that the sp. gr. is  $2.052$  at  $24^\circ/4^\circ$ ; and W. Biltz added that there is an expansion of  $2.44$  vols. when the hexammine is formed from ferrous iodide. The dissociation press.,  $p$  mm., was measured by F. Ephraim, and W. Biltz and G. F. Hüttig with the result that:

	$112^\circ$	$125^\circ$	$135.5^\circ$	$145.5^\circ$	$156.5^\circ$	$164^\circ$	$172.5^\circ$	$180.5^\circ$	$187.5^\circ$
$p$	62	88	115	180	276	355	477	625	800

The results are plotted in Fig. 602. W. Biltz said that the dissociation press. is  $150$  mm. at  $135^\circ$ . F. Müller gave  $50^\circ$  to  $182^\circ$  for the dissociation temp. G. Beck gave  $800$  cal. for the heat of formation. W. Biltz, and W. Biltz and G. F. Hüttig gave for the heat of formation ( $\text{FeI}_2 \cdot 6\text{NH}_3\text{gas}$ )  $=98.94$  Cals., or  $16.5$  Cals. per mol of ammonia; or ( $\text{FeI}_2 \cdot 2\text{NH}_3 \cdot 4\text{NH}_3\text{gas}$ )  $=58.0$  Cals., or  $14.50$  Cals. per mol of ammonia. Observations were also made by F. Ephraim. W. Biltz showed that the free energy of the reaction  $\text{FeI}_2 + 6\text{NH}_3\text{gas} = \text{FeI}_2 \cdot 6\text{NH}_3$ , at  $27^\circ$ , and atm. press., is  $42.06$  Cals., or  $7.01$  Cals. per mol of ammonia; and that the hexammine is a cation ammine which indicates that the structural formula is  $[\text{Fe}(\text{NH}_3)_6]\text{I}_2$ . F. Ephraim found that the hexammine retains its white colour in air, and is sensitive to light only when it loses ammonia. C. F. Jackson and I. H. Derby reported that the hexammine decomposes rapidly with the liberation of ammonia when it is exposed to air, but it remains unchanged in an atm. of ammonia, even at  $100^\circ$ ; it loses ammonia when heated in an indifferent gas, and forms a dark brown powder, of unknown composition—but contains 2 or 3 mols. of ammonia—which is stable in air; when exposed to the vapour of bromine, a large proportion, 70 to 71 per cent., is absorbed, and a mixture of ammonium ferric bromide, and

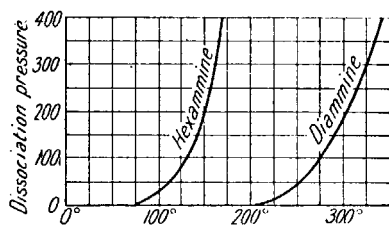


FIG. 602.—The Dissociation Pressures of the Ferrous Amminoiodides.

ferric ammonium pentabromiodide,  $\text{NiI}_4\text{FeI} \text{Br}_5$ , is formed. W. Biltz and G. F. Hüttig showed that when the hexammine is heated at about  $153^\circ$ , it passes into **ferrous diamminiodide**,  $\text{FeI}_2 \cdot 2\text{NH}_3$ , but no **ferrous monamminiodide** is formed. The dissociation press. of the diammine was found by W. Biltz and G. F. Hüttig to be 6.1, 12.1, and 85.4 mm. respectively at  $215^\circ$ ,  $231^\circ$ , and  $278^\circ$ ; and W. Biltz gave 100 mm. at  $287^\circ$ . F. Müller gave over  $350^\circ$  for the dissociation temp. of the diammine. W. Biltz and G. F. Hüttig found the heat of formation is  $(\text{FeI}_2 \cdot 2\text{NH}_{3\text{gas}}) = 40.92$  Cals., or 20.46 Cals. per mol of ammonia. W. Biltz observed that the free energy of the reaction  $\text{FeI}_2 + 2\text{NH}_{3\text{gas}} = \text{FeI}_2 \cdot 2\text{NH}_3$ , at  $27^\circ$ , and atm. press., is 21.46 Cals., or 10.73 Cals. per mol of ammonia; unlike the hexammine, the salt is not co-ordinative, and is regarded as a double salt. W. Hieber and E. Levy, and G. L. Clark studied the stabilities of the ammines. F. W. Bergstrom observed that no definite products are formed by the action of an ammonia soln. of potassium amide on ferrous iodide.

When a soln. of iodine and iron pentacarbonyl in dry ether is evaporated, W. Hieber and co-workers found that dark brown plates of **ferrous tetracarbonyl iodide**,  $\text{Fe}(\text{CO})_4\text{I}_2$ , are formed; and H. Hock and H. Stuhlmann prepared it by the action of  $\text{Fe}(\text{CO})_4\text{Hg}$  on a soln. of iodine in carbon disulphide. W. Hieber said that the salt is decomposed below 750 mm. at  $75^\circ$  into ferrous iodide and carbon monoxide. W. Hieber and co-workers found that the mol. wt. in nitrobenzene soln. is 430.4—theory for  $\text{Fe}(\text{CO})_4\text{I}_2$ , 421.3; the salt in nitrobenzene soln. slowly decomposes in sunlight; it is decomposed by water forming a soln. of ferrous iodide with the evolution of carbon monoxide; it forms complex salts,  $\text{FeCO}(\text{C}_5\text{H}_5\text{N})_2\text{I}_2$ , and  $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5\text{N})_2\text{I}_2$ , with pyridine. C. L. Jackson and I. H. Derby observed that ferrous iodide is reduced when it is heated to redness in **ethylene**, or in **acetylene**. J. W. Retgers found it to be almost insoluble in **methylene iodide**. F. Ephraim and R. Linn observed that ferrous iodide forms a complex with **methylaniline**,  $\text{FeI}_2 \cdot (\text{CH}_3 \cdot \text{NH}_2)_6$ ; H. M. Elsey, a complex with **ethylamine**, but it is insoluble in ethylamine, and soluble in **dimethylaminé**. R. E. Breuill, and W. Hieber and co-workers prepared a complex with **ethylenediamine**,  $[\text{Fe en}_3]\text{I}_2$ . C. L. Jackson and I. H. Derby observed that a complex is formed with **aniline**; H. Grossmann and F. Hünslér, a complex with **phenylhydrazine**,  $\text{FeI}_2(\text{C}_6\text{H}_5 \cdot \text{NHNH}_2)_6$ ; W. Hieber and co-workers, R. Weinland and co-workers, G. Spacu, and H. Hock and H. Stuhlmann, complexes with **pyridine**,  $\text{FeI}_2(\text{C}_5\text{H}_5\text{N})_6$ ,  $\text{FeI}_2(\text{C}_5\text{H}_5\text{N})_4$ , and  $\text{FeI}_2(\text{C}_5\text{H}_5\text{N})_2$ ; F. Blau, and A. Werner, a complex with  $\alpha\alpha'$ -**dipyridyl**,  $[\text{Fe}(\text{C}_{10}\text{H}_8\text{N}_2)_3]\text{I}_2 \cdot 5\text{H}_2\text{O}$ ; and it is optically active; and F. Blau, a complex with  $\alpha\alpha'$ -**phenanthroline**. C. L. Jackson and I. H. Derby found that ferrous iodide is soluble in **alcohol**. V. Thomas added that the alcoholic soln. absorbs nitric oxide. C. L. Jackson and I. H. Derby found ferrous iodide to be soluble in **glycerol**, and soln. of **sugar**. J. H. Long said that cane-sugar is inverted by ferrous iodide soln. T. Salzer, and A. Dupasquier studied the action of ferrous iodide on **starch**, and **cellulose** or filter paper. C. L. Jackson and I. H. Derby found that no perceptible chemical reaction occurs with **ether**; according to L. B. Parsons, ferrous iodide is insoluble in **carbon tetrachloride**, **carbon disulphide**, **chloroform**, **quinoline**, **pyridine**, **heptane**, **ethylbenzene** and **benzene**, and a little soluble in alcohol, ether, and **acetone**. B. Köhnlein observed no reaction with **propyl iodide**. A. Job and R. Reich observed that an ethereal soln. reacts with **zinc ethyl iodide** forming  $\text{FeC}_2\text{H}_5\text{I}$ . J. R. McKee and co-workers found that the soln. of ferrous iodide in **furfural** does not conduct electricity. C. L. Jackson and I. H. Derby said that no perceptible action was observed between ferrous iodide and benzene, **benzyl chloride**, **phenol**, or **hydroquinone**. C. Liebermann and H. Sachse, and P. Bruck recommended ferrous iodide as a carrier of iodine in organic reactions. C. Moureau and C. Dufrasse studied its action on the oxidation of **acrolein**. G. Champetier found that the reaction with **phenyl zinc bromide** can be represented by the equation:  $2\text{C}_6\text{H}_5\text{ZnBr} + 2\text{FeI}_2 \rightarrow 2\text{C}_6\text{H}_5\text{FeI} + \text{ZnBr}_2 + \text{ZnI}_2$ .

C. L. Jackson and I. H. Derby found that **mercury** has no action on ferrous

iodide when the two are ground together, or distilled together. Molten **silver** reduces ferrous iodide to iron. No reduction occurs by the action of nascent hydrogen from hydriodic acid and **zinc** or **iron**. C. Wagner and W. Preiss studied the induction of the reaction between **chromic acid** and iodides by ferrous salts.

**The complex salts of ferrous iodide.**—J. W. Retgers observed that no solid soln. or compounds separate from mixed soln. of **ammonium and ferrous iodides**. J. F. W. Johnston observed that an **auric ferrous iodide** separates from a mixed soln. of auric and ferrous iodides. J. B. Berthemot obtained a **mercuric ferrous iodide** by cooling a hot, mixed soln. of mercuric iodide and ferrous chloride; and P. A. von Bonsdorff, by the evaporation of a soln. of mercuric and ferrous iodides. A. Duboin found that the dark orange octahedra were **mercuric ferrous hexaiodide**,  $2\text{HgI}_2 \cdot \text{FeI}_2 \cdot 6\text{H}_2\text{O}$ . The sp. gr. is 4.04 at  $0^\circ$ . P. A. von Bonsdorff added that his product formed yellowish-brown needles, which oxidized readily, were decomposed by water, and were soluble in acetic acid, and in alcohol. According to A. Mosnier, ferrous iodide also forms a **lead ferrous hexaiodide**,  $\text{PbI}_2 \cdot 2\text{FeI}_2 \cdot 3\text{H}_2\text{O}$ , and likewise a complex salt with platinum iodide.

The higher iodide, **ferric iodide**,  $\text{FeI}_3$ , has not been isolated although it is probably contained in a soln. of ferrous iodide to which the proportion of iodine required for the tri-iodide has been added,  $2\text{FeI}_2 + \text{I}_2 = 2\text{FeI}_3$ . G. Kerner regarded the product as a soln. of iodine in aq. ferrous iodide because the solution gave most of the reactions of ferrous salts, and it gives a blue precipitate with potassium ferrocyanide which A. Oberdörffer showed is at first light blue, but becomes dark blue by the absorption of iodine. The precipitation of hydrated ferrous and ferric oxides by alkali hydroxide or carbonate from the mixed soln. of ferrous and ferric iodide obtained by mixing iodine and iron ( $3\text{Fe} + 4\text{I}_2$ ) with water, is attributed to the formation of complex ions  $\text{FeI}_3'$  from the union of  $\text{I}'$ -ions with ferrous iodide molecules; and the  $\text{FeI}_3'$ -ions are stable in the presence of ferric ions. E. Fleury says that the action of iodine on iron is inappreciable if the temp. be kept below  $15^\circ$ , but if the mixture be heated, ferric oxide is formed. A large excess of iodine is required to dissolve all the iron, and a large excess of iron is needed to convert the iodine into ferrous iodide. E. Fleury suggested that ferric iodide is first formed, and this is decomposed by heat into ferric oxide and hydriodic acid which then reacts with free iron to form ferrous iodide. G. Kerner showed that hydriodic acid dissolves recently-precipitated ferric hydroxide; the soln. smells of iodine, and gives the reactions characteristic of a ferrous salt and free iodine. The reaction is presumably:  $\text{Fe}_2\text{O}_3 + 6\text{HI} = 3\text{H}_2\text{O} + 2\text{FeI}_2 + \text{I}_2$ ; but J. Nicklès showed that if the ferric hydroxide be dissolved by hydriodic acid in the presence of ether, it does not give the reaction of a ferrous salt with potassium ferricyanide for some time. J. L. Lassaigne showed that the resulting yellowish-red soln. is resolved by heat into ferrous iodide and free iodine; and P. Squire, that although a soln. of ferrous iodide deposits ferric hydroxide when exposed to the air, the reaction is not analogous with that of the corresponding chloride:  $12\text{FeCl}_2 + \text{Aq.} + 3\text{O}_2 = 8\text{FeCl}_3 + 4\text{Fe}(\text{OH})_3$ , because the liquid still gives the reactions of a ferrous and not of a ferric salt. The subject was also discussed by J. J. Berzelius, J. M. Ordway, W. Spring, P. Nicolardot, J. Reitstötter, J. H. Mathews, H. Grossmann and F. Hünsele.

According to R. Abegg, and W. Maitland, the equilibrium constant of the reaction:  $2\text{Fe}^{++} + 2\text{I}^- \rightleftharpoons 2\text{Fe}^{+} + \text{I}_2$  is  $[\text{Fe}^{+}][\text{I}^-] = 0.00023[\text{Fe}^{++}]$  in the presence of solid iodine, so that when a ferric salt is treated with an alkali iodide, virtually all the iron in the solute forms iodine and ferrous iodide; the ferric iodide can be stable only in the presence of an enormous excess of ferrous iodide. K. Lialikoff and M. Bela found that the equilibrium depends on the degrees of ionization of the ferric, ferrous, and potassium iodides, but this effect becomes less important if the reaction takes place in 0.5*N*-potassium iodide soln. The equilibrium constant is profoundly changed by the presence of an acid, the extent of the alteration varying but slightly with the conc. of the acid. The equilibrium is displaced somewhat to



the right by the presence of either glycerol or methyl alcohol in 30 per cent. conc. The reaction was studied by J. N. Brönsted and K. Pedersen, and H. M. Dawson and E. Spivey; and E. K. Rideal and E. G. Williams studied the photochemical equilibrium. N. Sasaki added a soln. of barium iodide to one of ferric sulphate and observed that ferric iodide primarily formed decomposes rather slowly so that the freshly-prepared soln. is mainly one of ferric iodide. The electrical conductivity of the fresh soln. is nearly as great as a soln. of ferric chloride or bromide of the same concentration. The equilibrium is displaced in favour of ferric iodide by exposure to light. J. N. Brönsted and K. Pedersen studied the reaction between ferric chloride and potassium iodide at 25°, and obtained results in accord with the law of mass action for ionic equilibria. N. Sasaki represented the reaction:  $\text{Fe}^{+++} + \text{I}^- = \text{FeI}^{++}$ ;  $\text{Fe}^{+++} + 2\text{I}^- = \text{FeI}_2^+$ ;  $\text{FeI}^{++} = \text{Fe}^{+++} + \text{I}^-$ ;  $\text{FeI}_2^+ = \text{Fe}^{+++} + \text{I}^- + \text{I}^-$ ; and  $\text{I} + \text{I} = \text{I}_2$ , and A. von Kiss and I. Bossanyi found that on these assumptions, the reaction is unimolecular with respect to the ferric ions; and bimolecular for the iodine-ions. The hydrolyzed ferric-ions do not act with a measurable speed. The reaction is said to be ionic up to a concentration 0.15, and to obey the rule for neutral salts. Of the alkali iodides, only the sodium salt exerts a specific action. The chlorides of the uni- and bi-valent metals exert no marked influence; ferrous ions and sulphate ions slow down the reaction, whilst  $\text{H}^-$ ,  $\text{NO}_3^-$ ,  $\text{Br}^-$ , and  $\text{ClO}_3^-$  ions catalyze the action feebly.

G. B. Kistiakowsky found that the reaction  $2\text{Fe}^{+++} + \text{I}_3^- = 2\text{Fe}^{+++} + 3\text{I}^-$  is sensitive to radiations  $\lambda = 5460, 4360, \text{ and } 3660 \text{ \AA.}$  in the mercury spectrum; and E. K. Rideal and E. G. Williams observed that the reaction  $2\text{Fe}^{+++} + \text{I}_2 \rightleftharpoons 2\text{Fe}^{+++} + 2\text{I}^-$  is photosensitive to both ultra-violet and visible light, the latter within the range 5500 to 6500  $\text{\AA.}$ , with an apparent maximum at 5800  $\text{\AA.}$  The triiodide ion is the photosensitive constituent and the energy of excitation is equivalent to 2.14 volts, almost identical with the resonance potential of the iodine molecule. One quantum of absorbed radiant energy causes 1 mol. of iodine to react. The dark equilibrium constant,  $(\text{Fe}^{+++})(\text{I}_2)^{1/2}/(\text{Fe}^{+++})(\text{I}^-)$ , is 23.6 at 25°. The ratio of the velocity constant of the liberation of iodine at 35° to that at 25° is 2.713, whilst for the photochemical reaction this ratio is 1.17. The addition of potassium chloride increases the thermodynamic concentrations of all the reactants, increasing the velocity of reaction thereby, but not affecting the final equilibrium.

C. F. Möhr's observations that a very dil. soln. of ferric chloride (1 in 12,300) gives a blue colour on the addition of starch and potassium iodide only after a considerable time, depends on the fact that a soln. so much diluted is almost completely hydrolyzed and therefore only a very small proportion of iron can be present in the form of ferric ions; and the slow development of the blue coloration, owing to the formation of free iodine, is due to the reaction between the  $\text{I}^-$  ions and the  $\text{Fe}^{+++}$  ions from the hydroxide.

M. Berthelot gave for the heat of formation of ferric iodide ( $2\text{Fe}, 3\text{I}_{2\text{soln.}}, \text{Aq.}$ ) = 98.5 Cals.; ( $2\text{Fe}, 3\text{I}_{2\text{gas}}, \text{Aq.}$ ) = 139.1 Cals.; and  $(\text{Fe}_2\text{O}_{3\text{ppd.}}, 6\text{HI}) = 33.2 \text{ Cals.}$  Observations were made by T. Andrews. The subject was studied by E. Rabino-witsch and E. Thilo. A. K. Chapman measured the emission spectral lines of ferric iodide. L. Riéty measured the potential of soln. entering and leaving a capillary tube. E. Beckmann estimated from the effect on the b.p. of iodine that ferric iodide is present in iodine soln. in doubled molecules,  $\text{Fe}_2\text{I}_6$ ; J. Timmermans, and E. Beckmann's observations on the effect of the salt on the f.p. of iodine were unsatisfactory because of the low solubility of the salt. L. Carius and J. A. Wanklyn found that when a mixture of ferrous iodide and iodine is heated to the temp. at which iodine is evolved, then, on cooling, a temp. is attained at which iodine is copiously evolved. W. Manchot and O. Wilhelms said that in the reaction between potassium iodide, hydrogen dioxide, and ammonium ferrous sulphate, an **iron pentaiodide**,  $\text{FeI}_5$ , is formed as a transient intermediate compound. J. Nicklès obtained what he regarded as ferric iodide by the action of hydriodic acid in ethereal soln. on ferrous iodide, and noted that the soln. dissolves metallic gold. E. C. Franklin

and C. A. Kraus say that ferric iodide (probably ferrous iodide) is very soluble in liquid ammonia. P. T. Walden did not succeed in preparing complex salts of ferric iodide with other metal iodides. K. Jablczynsky and M. Stückgold examined the reaction between ammonium ferrous iodide and iodine, and found that combination occurs to the extent of 72 per cent. at ordinary temp.; and the speed of reaction is 4.5 times as great as the reverse reaction—decomposition of ferric iodide. This is taken to mean that the iodometric titration of ferric iron is inaccurate.

K. Seubert and A. Dorrer found that a mixture of dil. soln. of ferric chloride and potassium iodide give a yellowish-brown coloration, much deeper than a soln. of ferric chloride of corresponding concentration, and they assume that an unstable **ferric dichloriodide**,  $\text{FeICl}_2$ , is formed:  $\text{FeCl}_3 + \text{KI} \rightleftharpoons \text{FeICl}_2 + \text{KCl}$ , and that a neutral aq. soln. of ferrous chloride and alcoholic iodine owes its brownish-red colour to the same compound. It is not ferric hydroxychloride,  $\text{FeCl}_2(\text{OH})$ , because the soln. deposits iodine when diluted with water. For **ammonium ferric pentabromiodide**,  $\text{NH}_4\text{FeBr}_5\text{I}$ , *vide supra*.

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#### § 40. The Iron Sulphides—Ferrous Sulphide and Pyrrhotite

The *pyrites fuscus lamellosus* of J. G. Wallerius<sup>1</sup> was called by J. B. L. Romé de l'Isle *pyrites* or *marcassites rhomboïdales*, and he described the hexagonal crystals. A. G. Werner called it *Magnetkies*; R. Kirwan, *magnetic pyrites*; W. Phillips, *magnetic iron pyrites*; R. J. Haüy, *fer sulfuré magnétique*—vulgairement *pyrite magnétique*; C. C. Leonhard, *Leberkies*; F. S. Beudant, *Leberkise*; W. Haidinger, *pyrrhotin*—from *πυρρός*, reddish; and J. D. Dana, *pyrrhotite*. The iron sulphide found in meteorites and named by W. Haidinger *troilite*—after D. Troili—is considered by G. Linck, S. Meunier, and others to be pyrrhotite. Both forms are ferrous sulphides containing a small excess of sulphur in solid soln., and, as emphasized by G. A. Kenngott, and T. Petersen, their principal difference is in their magnetic properties. D. Forbes described a nickeliferous variety which M. F. Heddle called *inverarite*—from its occurrence in Inverary, Argyleshire; D. Forbes named a variety from the eastern slope of the Andes *kræberite*—after P. Kræber; and A. Knop, called a variety from Horbach, in the Black Forest, *horbachite*. C. W. Blomstrand described a variety from Nya-Kopparberg, Sweden, and he called it *Vallerite* or *Wallerite*—after J. G. Wallerius; J. Petréň regarded it as a mixture of different minerals. As indicated below, pyrrhotite contains a variable proportion of sulphur. To summarize, if pyrrhotite be included in the general term *pyrites*:

PYRITES	cubic crystals	.	.	.	.	.	pyrite
	rhombic crystals	.	.	.	.	.	marcasite
	rhombohedral crystals—magnetic	.	.	.	.	.	pyrrhotite

**The nature of ferrous sulphide and of the pyrrhotites.**—According to E. T. Allen<sup>2</sup> and co-workers, "pure ferrous sulphide has never been made," except, presumably, by chance. Analyses of pyrrhotite were reported by A. Hilger, M. Toumaire, T. Scheerer, A. Raimondi, H. How, B. J. Harrington, F. Ehrenheim, and numerous others. The nickel and cobalt contents of pyrrhotite were discussed by C. W. Dickson, H. Schneiderhöhn, E. Weinschenk, M. F. Heddle, D. Forbes, J. D. Dana, and W. Campbell and C. W. Knight.

The analyses of pyrrhotite show a more variable ratio for Fe : S than is the case with the other forms of iron sulphide. Thus, F. Stromeyer gave  $\text{Fe}_3\text{S}_4$ , for the composition of a sample from Barèges. T. Sidot's synthesis of this **ferrosic sulphide**,  $\text{Fe}_3\text{S}_4$ , analogous to magnetite,  $\text{Fe}_3\text{O}_4$ , indicated below, is questioned by C. Fontana, and W. F. de Jong and H. W. V. Willems. A. Stelzner gave  $\text{Fe}_4\text{S}_5$ , for the composition of a sample from Himmelstürst, Freiberg; while samples analyzed by F. Stromeyer, H. V. Regnault, P. Berthier, C. F. Rammelsberg, I. Domeyko, and E. Manasse corresponded with  $\text{Fe}_5\text{S}_8$ ; C. F. Plattner, C. F. Rammelsberg, T. Petersen, and G. Lindström gave results agreeing with  $\text{Fe}_6\text{S}_7$ ; J. Akermann, C. F. Rammelsberg, G. Lindström, H. Hahn, H. Habermehl, A. Funaro, A. Stelzner, W. Irmer, G. Rose, J. J. Berzelius, G. Nyiredy, and W. J. Sharwood, with  $\text{Fe}_7\text{S}_8$ ; K. Bornemann and O. Hengstenberg, H. Rose, C. F. Rammelsberg, L. Michel, P. Berthier, F. M. Baumert, G. Lindström, G. H. F. Ulrich, and J. D. Dana, with  $\text{Fe}_8\text{S}_9$ ; E. Schumacher, C. Doelter, N. von Leuchtenberg, C. Bodewig, and M. F. Heddle, with  $\text{Fe}_9\text{S}_{10}$ ; F. von Schaffgotsch, C. F. Rammelsberg, and G. Lindström, with  $\text{Fe}_{10}\text{S}_{11}$ ; J. Middleton, C. F. Rammelsberg, G. Lindström, C. Bodewig, L. F. Nilson, J. Thiel, J. D. Dana, F. von Schaffgotsch, M. Palfy, E. Arbeiter, A. Serra, A. Bianchi, and E. Glatzel, with  $\text{Fe}_{11}\text{S}_{12}$ ; L. Bucca, C. Doelter, and R. Lorenz, with  $\text{Fe}_{12}\text{S}_{13}$ ; and G. Lindström, G. A. Kenngott, C. S. Schiffner and co-workers, R. Brauns, V. Zeleny, C. Hatchett, C. W. Dickson, W. J. Sharwood, and A. Serra, with  $\text{FeS}$ . The analyses of a sample of troilite from meteorites gave S. Meunier  $\text{Fe}_4\text{S}_5$ ,  $\text{Fe}_5\text{S}_7$ , and  $\text{Fe}_6\text{S}_8$ ; J. L. Smith,  $\text{Fe}_8\text{S}_9$ ; and J. L. Smith, C. F. Rammelsberg, I. Domeyko, G. Nauckhoff, F. E. Geinitz, C. Winkler, S. M. Losanitsch, J. Schilling, W. Flight, E. Cohen, O. A. Derby, W. Tassin, L. H. Borgström, and W. Ramsay and L. H. Borgström studied the subject. The analyses of artificial pyrrhotite gave J. J. Berzelius, C. F. Rammelsberg, F. Stromeyer, J. A. Arfvedson, B. G. Bredberg, A. S. Eakle, L. Bucca, C. Doelter, and R. Lorenz results ranging over  $\text{Fe}_2\text{S}_3$  (*vide infra*),  $\text{Fe}_3\text{S}_4$ ,  $\text{Fe}_4\text{S}_5$ ,  $\text{Fe}_7\text{S}_8$ ,  $\text{Fe}_8\text{S}_9$ ,  $\text{Fe}_{10}\text{S}_{11}$ ,  $\text{Fe}_{12}\text{S}_{13}$ , and  $\text{FeS}$ —*vide infra*, R. Juza and W. Biltz in connection with pyrites. They could find only  $\text{FeS}$  and  $\text{FeS}_2$ , not the intermediate forms.

F. Stromeyer found that a residue of sulphur remained when pyrrhotite is dissolved in hydrochloric acid, and supposed that it consists of ferrous sulphide mixed with pyrites; and this view was supported by J. J. Berzelius, C. Doelter, L. Gedel, and A. Knop. M. Leo also found specimens of pyrrhotite with inclusions of pyrite; and E. Wildschrey noted a number of occurrences of pyrrhotite in the neighbourhood of deposits of pyrite. The hypothesis was condemned by the fact that F. von Schaffgotsch, G. Rose, H. Habermehl, and E. Posnjak and co-workers found that when the mineral is dissolved in acids, sulphur, not pyrites, remains; and E. Arbeiter found that pyrrhotite gives off sulphur at a higher temp. than does pyrite. F. von Schaffgotsch, E. Arbeiter, C. W. Blomstrand, G. Cesaro, and R. Scheuer favoured the assumption that pyrrhotite is a mixture of ferric sulphide,  $\text{Fe}_2\text{S}_3$ , and ferrous sulphide,  $\text{FeS}$ . P. Niggli considered it to be a polysulphide. C. F. Plattner observed a loss of sulphur when pyrrhotite is heated in hydrogen and a residue of ferrous sulphide remained. J. J. Berzelius, and likewise also C. F. Rammelsberg, suggested that the sulphides represented by  $\text{Fe}_7\text{S}_8$  may exist in two forms:  $6\text{FeS}.\text{FeS}_2$ , and  $5\text{FeS}.\text{Fe}_2\text{S}_3$ ; whilst F. von Schaffgotsch gave  $\text{FeS}.\text{Fe}_2\text{S}_3$ ,  $5\text{FeS}.\text{Fe}_2\text{S}_3$ , and  $9\text{FeS}.\text{Fe}_2\text{S}_3$ ; and G. Rose,  $5\text{FeS}.\text{Fe}_2\text{S}_3$ . A. Breithaupt, M. L. Frankenheim, F. von Kobell, and T. Petersen assumed that pyrrhotite is, in the ideal case, ferrous sulphide which may be isomorphous with millerite, and nickelite. T. Sidot concluded from the production of pyrrhotite from magnetite and hydrogen sulphide that its formula is  $\text{Fe}_3\text{S}_4$ ; C. Bodewig, E. Glatzel, and C. Doelter gave the formula  $\text{Fe}_{11}\text{S}_{12}$  which was regarded as a complex  $10\text{FeS}.\text{FeS}_2$ ,

and not  $9\text{FeS} \cdot \text{Fe}_2\text{S}_3$  because of the isomorphism of pyrrhotite with wurtzite. G. Cesaro, H. Habermehl, and C. F. Rammelsberg represented pyrrhotite by  $\text{Fe}_n\text{S}_{n+1}$ , or  $\text{Fe}_2\text{S}_3(n-2)\text{FeS}$ , when the analyses ranged from  $\text{Fe}_5\text{S}_6$  to  $\text{Fe}_{16}\text{S}_{17}$ . G. Cesaro assumed that the molecule contained two  $\text{S}=\text{Fe}-\text{S}$  groups, so that  $\text{Fe}_{11}\text{S}_{12}$  was represented by the chain formula:  $\text{S}=\text{Fe}'''-\text{S}-(\text{Fe}_9''\text{S}_8)-\text{S}-\text{Fe}'''=\text{S}$ .

E. Glatzel favoured the formula  $\text{FeS}$ , and he based his opinion on the results of 70 analyses, 66 of which agreed well with the formula  $\text{FeS}$ . The reviews of the analytical data by G. Lindström, and by H. Habermehl indicated that pyrrhotite is a homogeneous compound of variable composition. At that time, homogeneous solids of variable composition were anomalous. To-day, homogeneous solids of this type are fairly common and they are called solid soln. or isomorphous mixtures. F. von Schaffgotsch, C. Bodewig, and H. Habermehl showed that pyrrhotite contains no free sulphur accessible to the solvent effect of carbon disulphide. E. T. Allen and co-workers tested the hypothesis that the various pyrrhotites are solid soln. of sulphur in ferrous sulphide. They prepared various pyrrhotites by the thermal decomposition of pyrite or marcasite, or by heating iron in sulphur vapour—*vide infra*. The composition of the product formed at any temp. depends on the press. of the sulphur vapour; the maximum percentage obtained at  $600^\circ$  was 6.04, and by extrapolation, pyrrhotite with 6.5 per cent. of sulphur, the maximum proportion found in natural pyrrhotites, would be formed at  $565^\circ$ . The formula of pyrrhotite is therefore represented  $(\text{FeS})_n$ , or, according to P. Niggli,  $n\text{FeS} \cdot m\text{S}$ . F. Zambonini, J. Jakob, and W. F. de Jong and H. W. V. Willems also agreed with the view that pyrrhotite is a solid soln. of ferrous sulphide and sulphur; and the hypothesis is in harmony with the X-radiograms of C. Fontana—*vide infra*. According to L. S. Ramsdall, the excess sulphur in pyrrhotite is accompanied by a decrease in the size of the unit cell, and a lowering of the density; and these facts are taken to indicate a replacement of Fe by S, rather than an addition of more S. J. H. L. Vogt stated that when melted with the sulphides of other heavy metals, ferrous sulphide is present in soln. as simple molecules.

A number of **iron subsulphides** has been reported; thus, J. A. Arfvedson<sup>3</sup> obtained  $\text{Fe}_8\text{S}$ , as a greyish-black powder by reducing red-hot ferric sulphate in hydrogen; J. A. Arfvedson, L. Playfair and J. P. Joule, A. Murlot, and P. Berthier,  $\text{Fe}_2\text{S}$ , by reducing ferrous sulphate in hydrogen, and by fusing a mixture of iron and ordinary iron sulphide in a graphite crucible; and A. Gautier and L. Hallopeau, L. Michel, and H. N. Warren,  $\text{Fe}_4\text{S}_3$ , by heating iron to  $1300^\circ$  to  $1400^\circ$  in an atm. of the vapour of carbon disulphide, and cooling the product in the same atmosphere. J. B. Peel and co-workers obtained a partially-fused product of variable composition—average  $\text{Fe}_7\text{S}_6$ . The sp. gr. of the crystalline mass was 6.96; it did not alter on exposure to air; it was oxidized with difficulty; and was soluble in dil. acids with the evolution of hydrogen and hydrogen sulphide. H. N. Warren found that if iron which has been fused with a small proportion of sulphur be made the anode, with a dil. soln. of ferrous chloride as electrolyte, then on electrolysis, iron is deposited on the cathode of copper or platinum, and in a few hours, the black, granular precipitate on the anode may be detached. It is ferrous sulphide,  $\text{FeS}$ . This is taken to mean that  $\text{FeS}$  is the only compound formed by the simple action of sulphur on metallic iron, aided by heat, and that the sulphur does not disseminate itself throughout the whole mass of metal to form a compound possessing a formula where iron predominates largely, such as would be inferred from the formula expressed by  $\text{Fe}_8\text{S}$ ; but exists rather in the form of sulphide or iron, disseminated, so to speak, through a mass of pure iron, the sulphide present forming a simple network allowing the current free passage; the iron being a much better conductor of electricity than the sulphide, becomes more rapidly dissolved, leaving the residual sulphide. E. V. Britzke and A. F. Kapustinsky, and K. Jellinek and J. Zakowsky discussed the affinity of sulphur for iron.

H. le Chatelier and A. Ziegler obtained no evidence of the formation of a subsulphide in the regulus obtained by melting together iron and ferrous sulphide.

Under the microscope, the product appears as a mixture of the two components. J. E. Stead described the microstructure of the products obtained by melting different proportions of sulphur with iron (*q.v.*). R. Scheuer observed that in some cases, the mixtures of iron and ferrous sulphide appear homogeneous, and they cannot be separated into their constituents by a magnet. Observations on the subject were also made by G. P. Schweder. W. Treitschke and G. Tammann constructed a thermal diagram for a mixture of iron and ferrous sulphide (Figs. 604 and 605); they found that ferrous sulphide and iron are not completely miscible in the fused condition, mixtures containing 8 to 80 per cent. of ferrous sulphide separating into two layers at 1400°. The f.p. curve falls from 1540°, the f.p. of iron, to 1400°, remains horizontal until the disappearance of the layer rich in iron, then falls to the eutectic temp., 970°, and finally rises to 1300°, the f.p. of ferrous sulphide. The eutectic mixture contains about 16 per cent. of the sulphide. The components separate to a great extent in the form of two sat. mixed crystals, containing 3 and 96 per cent. by weight of iron respectively. After crystallization is complete, secondary changes due to polymorphous transformations of the components take place. Pure iron shows two transition points at 855° and 760°, corresponding with the transformation of  $\gamma$ - to  $\beta$ -iron and  $\beta$ - to  $\alpha$ -iron respectively; the first of these is lowered to a greater extent than the second by the presence of ferrous sulphide, and with less than 92 per cent. of iron there is only one break in the cooling curve at 800°, which is probably connected with the solubility of ferrous sulphide in  $\gamma$ -iron. There is some evidence to show that when the temp. of mixtures rich in iron falls to about 800°, the mixed crystals undergo partial separation into their components. At 130° occurs the transition of  $\beta$ FeS, observed by H. le Chatelier and A. Ziegler; it is attended by a considerable dilation. The deleterious effect of traces of sulphur on the properties of iron is discussed in the light of the above results. In mixtures containing more than 2 per cent. of sulphur, this effect is due to the presence of a readily fusible layer of sulphide between the particles of iron. That the presence of even 0.02 per cent. of sulphur is disadvantageous is to be ascribed to the brittle character of the mixed crystals rich in iron. The transformation at about 130° was investigated by F. Rinne and H. E. Boeke—*vide infra*—they said that at 138° the solid soln. has 7 per cent. of iron as a maximum, and R. Loebe and E. Becker said 1 per cent. of iron at 985°. The structure was discussed by H. Rheinboldt.

K. Friedrich obtained rather simpler results, no separation into layers was observed at 1400° with mixtures containing 8 to 80 per cent. Fe. This was confirmed by F. H. Edwards, R. Loebe and E. Becker, and B. Bogitsch, who found that the f.p. curve, Fig. 603, is simple, and has a eutectic at 985° and 84.6 per cent. FeS. Observations were made by R. Juza and co-workers. A. Fry found the solubility of sulphur in  $\gamma$ -iron is 0.025 per cent., and A. Ziegler gave 0.03 per cent. K. Miyazaki said that the eutectic point is at 985° and 83 per cent. FeS. The solid components on the iron side of the eutectic are virtually immiscible, whilst the ferrous sulphide retains about 1 per cent. of iron in solid soln. K. Miyazaki found for the liquidus curve:

FeS . .	0	10.33	20.90	32.47	51.49	71.39	80.84	88.28	98.63 per cent.
F.p. . .	1530°	1445°	1409°	1370°	1335°	1175°	1035°	1056°	1183°

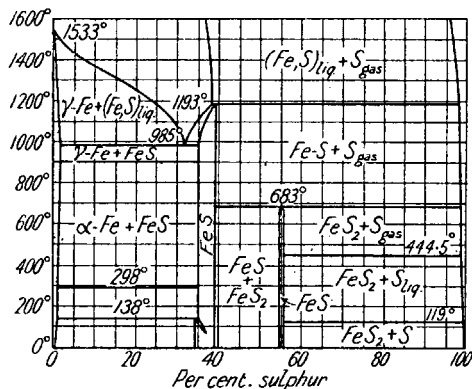
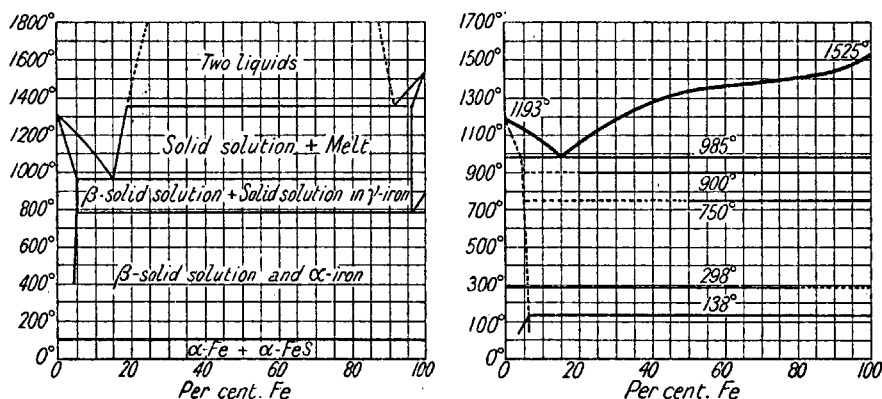


FIG. 603.—Equilibrium Diagram of the System: Fe-S.

C. Benedicks and H. Löfquist's equilibrium diagram of the whole system Fe-S is shown in Fig. 604. C. Benedicks observed that a break is produced in the liquidus curve of the system Fe-FeS by the presence of a third component which is more soluble in one of the pure components than is the mixed mass. For instance, a break is produced by silicon in the liquidus curve of iron and ferrous sulphide, which are normally totally miscible. Silicon is readily soluble in molten iron, but sparingly soluble in molten ferrous sulphide. W. P. Jorissen and B. L. Ongkie-hong studied the limits of the reaction between iron and sulphur, and the effect of silica on the results. R. Loebe and E. Becker found that the ferrous sulphide has no influence on the transformation points of iron. A polymorphic transformation of ferrous sulphide occurs at  $298^{\circ}$ ; and the transformation at  $138^{\circ}$  was observed with all mixtures containing over 7 per cent. of iron. The brittleness of iron containing sulphide is attributed to this transformation. The eutectic tends to become segregated in mixtures rich in sulphide. Alloys which have been in contact with oxygen contain a new eutectic. Fusion of iron sulphide with iron oxide, however, leads to the elimination of sulphur and formation of ferrite, and the structure is better developed by fusing the sulphide in contact with air.



FIGS. 604 and 605.—Freezing-point Curves of the System : Fe-FeS.

The composition of the eutectic is uncertain. The brittleness of iron containing sulphur at a red-heat is due to the absorption of oxygen in this form. The effect of sulphur on cast iron has been previously considered; F. Wüst and R. Pütz found that the presence of sulphur lowers the solubility of carbon in iron; and E. Piwowarsky and F. Schumacher showed that the effect of sulphur is greater the lower are the carbon and silicon contents of the iron. The subject was investigated by K. Schönrock. D. M. Levy, and T. Liesching studied the ternary system : Fe-S-C, and the former found a ternary eutectic with 2.4 to 4 per cent. of carbon, and 0 to 1.4 per cent. of sulphur. T. Liesching found that the eutectic between iron and carbon is lowered  $40^{\circ}$  for each per cent. of sulphur.

A. Lacroix<sup>4</sup> observed pyrrhotite amongst the substances produced during the eruption of Vesuvius in April, 1906; and troilite, found in meteorites, as previously indicated, frequently approximates in composition to that of **ferrous sulphide**, FeS. P. Tschirwinsky found that the troilite in 81 strong meteorites averaged 5.56 per cent. As shown by E. T. Allen and co-workers, E. Manasse, etc., pyrrhotite also occurs in meteorites. Many occurrences of pyrrhotite also approach ferrous sulphide in composition.

Pyrrhotite is not uncommon, though it is only a minor constituent of igneous rocks, and a similar remark applies to pyrite, but pyrrhotite is more characteristic of the ferromagnesian rocks like gabbro, diabase, diorite, norite, augite, and basalt. It often occurs mixed with other pyrites, and, according to A. A. Julien,<sup>5</sup> occurs in clay slates, mica slates, and in rocks of incipient metamorphism—*e.g.*, in beds of

limestone that have escaped conversion into marble prevailing in adjacent districts. J. H. L. Vogt regarded some pyrrhotite deposits of Norway as direct segregations from silicate magmas. R. Brauns described pseudomorphs of pyrrhotite after pyrite in the shales of Finkenberga, showing that the former was produced from the latter; similar results were observed by W. Eitel, in the basalts of Kassel; O. Mügge, in the shales of Weitisberga; G. Frebold, in the gabbro of Radau, Harz; P. J. Shenon, in sphalerite; C. L. Sagui and A. Jourdan, in the Bottino mine (Florence); and by E. Wildschrey, in the basalts of the Siebengebirges. H. Schneiderhöhn, and F. Wernicke discussed the paragenesis of pyrrhotite, pyrite, and marcasite. E. Harbort attributed the pyrrhotite in the salts of Aller-Nordstern to the formation of iron sulphate by the action of the carnallite on the iron chloride in the salts, and the subsequent reduction of the sulphate to pyrrhotite by the bituminous matters there present. The reduction of iron sulphate to sulphide by organic matter in natural waters was discussed by J. J. Berzelius, and M. E. Chevreul. C. Wurm observed iron intimately associated with the pyrrhotite.

**The formation and preparation of ferrous sulphide and pyrrhotite.**—Pyrrhotite has been occasionally reported as a furnace product; thus, J. F. L. Hausmann,<sup>6</sup> and C. W. C. Fuchs found it in prismatic crystals in a Harz furnace; L. Bucca, in a Catania furnace; J. H. L. Vogt, in blast-furnace slags; F. Cornu, in a cinder-heap at Bilin; C. W. Carstens, in a copper matte; C. Reidemeister, in cast-iron retorts used in purifying sulphur; and J. Michael, in preparing alkali bromide from iron bromide and alkali sulphide. M. E. Chevreul found some sulphide *sous le pavé des villes*.

The affinity of sulphur for iron was discussed by C. Frick,<sup>7</sup> and O. Ruff and B. Hirsch; and G. Tammann and K. Schaarwächter found that when an excess of iron mixed with sulphur is heated, there is a marked evolution of heat at 210°, and the temp. then rises rapidly to about 500°. C. W. Scheele, and N. Sokoloff showed that when a mixture of iron-filings and sulphur is heated, it glows vividly and forms a chemical compound, ferrous sulphide, FeS. According to A. Evain, V. Merz and W. Weith, and J. G. Gahn, when a stick of sulphur is pressed against a plate of red-hot bar iron, not cast iron, the plate is perforated, and iron sulphide is formed; the reaction between the two elements is faster with steel. The reaction was found by F. P. Dunnington to proceed rapidly with raw iron, but A. Evain added that cast iron does not react. W. P. Jorissen and C. Groeneveld said that with a mixture of equal parts of iron and sulphur, the reaction started at one point travels uniformly in different directions; but the reaction is so propagated throughout the mass only with mixtures having between 45.4 and 86.7 per cent. of iron.

J. J. Berzelius, C. Hatchett, L. Gedel, C. F. Rammelsberg, R. Winderlich, G. P. Schweder, and R. Scheuer obtained ferrous sulphide by heating strips of iron with sulphur, not in excess, contained in a crucible, and bending the strips of iron to separate the sulphide. If heat be applied too vigorously, the sulphur fuses with the rest of the iron; and if the sulphur be in excess, pyrite may be formed. The products may approximate FeS in composition, or they may appear as pyrrhotite, that is, as a solid soln. of sulphur in ferrous sulphide. J. L. Proust, C. F. Rammelsberg, and B. G. Bredberg obtained the sulphide by heating in a covered crucible of fireclay or cast iron, a mixture of iron-filings with two-thirds their weight of sulphur; and K. Bornemann, and C. N. Schuette and C. G. Maier melted a mixture of iron with an excess of sulphur in a graphite crucible, under a layer of wood-charcoal, and obtained ferrous sulphide of a high degree of purity. K. Jellinek and J. Zakowsky recommended heating a mixture of sulphur with twice its weight of iron, and afterwards mixing the product with sulphur and heating it in a current of hydrogen. An analogous process was employed by E. Jordis and E. Schweizer, and K. Miyazaki—*vide supra*, Figs. 604 and 605. E. T. Allen and co-workers prepared pyrrhotite by the direct union of iron and sulphur, and added that any excess of sulphur enters into solid soln. with the ferrous sulphide. In meteorites,



the excess of iron renders possible the formation of the monosulphide alone, as troilite. P. Chirvinsky observed that the reactions taking place in the formation of the meteorites are:  $6\text{Fe} + 3\text{O} + \text{S} = 6\text{Fe} + \text{SO}_2 + \text{O} = 2\text{Fe} + 3\text{FeO} + \text{FeS}$ . Oxidation of iron by oxygen occurs only after complete oxidation of silicon and manganese has taken place, whilst sulphur shows a relatively greater affinity for iron, forming troilite, which on account of its lower f.p. fills the veins and cracks. The black veins in the stone meteorites consist of josite,  $\text{FeO}$ , and troilite, with scorified silicate material and some iron. The ferrous oxide-ferrous sulphide eutectic, m.p.  $1060^\circ$ , may also be formed. The reaction  $3\text{Fe} + \text{SO}_2 = \text{FeS} + 2\text{FeO}$  is exothermic, and proceeds from left to right at fairly low temp.

C. F. Rammelsberg observed that at a low temp. iron disulphide is formed, as the temp. rises, ferric sulphide appears, and at a still higher temp., ferrous sulphide. Analogous observations were made by R. Scheuer, and H. N. Warren. According to L. Gedel, if iron mixed with an excess of sulphur be heated to  $450^\circ$ , or  $500^\circ$ , iron disulphide is formed; at  $700^\circ$ , the product has a composition  $\text{Fe}_7\text{S}_8$ ; and above  $700^\circ$ ,  $\text{FeS}$ . W. Treitschke and G. Tammann said that for ferrous sulphide, the temp. should be raised to  $1400^\circ$ . A. W. Hofmann observed that iron burns with vivid incandescence in the vapour of sulphur, and N. Juschkevitch added that the vapour begins to act on iron at about  $700^\circ$  forming ferrous sulphide mixed with an excess of sulphur; a similar product is obtained by melting a mixture of iron and sulphur at  $1220^\circ$  in a current of hydrogen. These products yield ferrous sulphide when they are heated with sulphur for 2 hrs. in a current of nitrogen at  $1220^\circ$ . W. Spring found that under a press. of 6500 atm., a powdered mixture of eq. proportions of iron and sulphur forms a homogeneous mass of ferrous sulphide which gives off hydrogen sulphide when treated with acids; with an excess of sulphur, polysulphides are similarly produced. K. Brodowsky studied the joint action of heat and press. on a mixture of iron and sulphur. R. Lorenz stated that if ferrous sulphide be heated with ammonium chloride, well-formed, black, shining crystals of ferrous sulphide appear in the upper part of the crucible.

K. Hilgenstock, A. Ledebur, and N. Juschkevitch obtained ferrous sulphide by the action of hydrogen sulphide on iron between  $400^\circ$  and  $500^\circ$ ; J. B. Peel and co-workers recommended  $538^\circ$ ; and F. Gieseler,  $700^\circ$ . J. Jahn, and F. Schmitz studied the speed of the reaction between iron and hydrogen sulphide at temp. between  $100^\circ$  and  $414^\circ$ . R. Lorenz, E. T. Allen and co-workers, W. G. Mixer, L. Moser and E. Neusser, and S. Meunier obtained crystals of troilite by heating iron to redness in a current of hydrogen sulphide; and J. B. Peel and co-workers obtained silver-white, crystalline, non-magnetic ferrous sulphide of sp. gr. 4.630 by the action of hydrogen sulphide on iron at  $1000^\circ$ . Iron sulphide is also formed by the action of other sulphides on iron; thus, E. Priwoznik found this to be the case with ammonium polysulphides; G. P. Schweder, and G. Tammann and H. Bohner, with cuprous sulphide; R. Lorenz, by the electrolysis of a soln. of potassium chloride with an iron anode and a cathode of cupric sulphide; L. E. Martin, with a soln. of strontium or barium sulphide at  $40^\circ$  to  $50^\circ$ . H. G. S. Anderson, with zinc sulphide; and H. von Jüptner, with lead sulphide. A. Cavazzi found that finely-divided iron, reduced in hydrogen, reacts with carbon disulphide at a red-heat forming ferrous sulphide and graphitic carbon. G. A. Shakhoff and co-workers prepared the sulphide by heating iron in sulphur dioxide in the presence of carbon or carbon monoxide. O. Loew heated iron-filings, water, and carbon disulphide in a sealed tube at  $100^\circ$ , and obtained ferrous sulphide and iron formate. The reaction was discussed by K. Hilgenstock. S. Hilpert and E. Colver-Glauert, K. Hilgenstock, and A. Ledebur observed that sulphur dioxide acts on heated iron forming ferrous sulphide, sulphite, and thiosulphate. A. de Hemptinne found that 62 per cent. sulphuric acid is reduced by iron forming ferrous sulphide. F. Projahn, and L. Hackspill and R. Grandadam observed that at about  $1000^\circ$ , alkali sulphates form ferrous sulphide and ferric oxide; R. Finkener, and K. Hilgenstock, that calcium sulphate forms calcium sulphide and oxide; and

N. W. Fischer, that a mixture of equal parts of iron-filings and charcoal, with twice its weight of lead sulphate, forms lead, and ferrous sulphide. J. Tscherniak and H. Günzburg observed that a mixture of iron, potassium thiocyanate, lime, and carbon also furnishes ferrous sulphide.

K. Brückner, E. Mandowsky, J. L. Proust, C. F. Rammelsberg, R. Scheuer, O. Schumann, T. Sidot, and N. Sokoloff observed that when a mixture of ferric oxide and sulphur is heated, some pyrrhotite or ferrous sulphide and sulphur dioxide are formed; H. Rose passed hydrogen over the heated mixture and obtained analogous results. R. Winderlich employed an excess of sulphur and obtained *reines Eisensulfid*. If hydrogen sulphide alone or mixed with hydrogen chloride be passed over ferric hydroxide, L. Gedel observed that ferrous sulphide and sulphur—as well as some iron disulphide—are formed. L. A. Sayce also noted that ferrous sulphide is formed by the action of hydrogen sulphide on hydrated ferric oxide below  $100^{\circ}$ —*vide supra*, ferric oxide. A. Gautier, and L. A. Sayce observed that at a red-heat, or, according to M. Picon at  $900^{\circ}$ , the reaction can be symbolized:  $2\text{Fe}_2\text{O}_3 + 7\text{H}_2\text{S} = 4\text{FeS} + 3\text{SO}_2 + 7\text{H}_2$ . L. Moser and E. Neusser obtained crystals of the sulphide by heating iron or its oxide in a current of hydrogen and hydrogen sulphide in the proportion 5:1. K. Hilgenstock, and A. Ledebur studied the influence of temp. on the reaction. J. Dewar and H. O. Jones, and K. Hilgenstock obtained ferrous sulphide by the action of carbon disulphide on ferric oxide at a red-heat; O. W. Gibbs, by heating to redness a mixture of ferric oxide and sodium thiosulphate; and J. Tscherniak, by the action of thiocyanates on ferric oxide. Ferrosic oxide behaves similarly; thus, H. Rose passed hydrogen over a red-hot mixture of ferrosic oxide and sulphur, and obtained ferrous sulphide; and C. Fontana showed that the product at a white-heat approximates  $\text{Fe}_3\text{S}_4$ , the sulphur analogue of magnetite,  $\text{Fe}_3\text{O}_4$ . The X-radiograms indicate that the  $\text{Fe}_3\text{S}_4$  is really a solid soln. of ferrous sulphide and sulphur. T. Sidot and C. Friedel, C. Fontana, A. Gautier, and R. Scheuer observed that ferrous sulphide is formed, in yellow, hexagonal crystals when hydrogen sulphide is passed over red-hot ferrosic oxide:  $\text{Fe}_3\text{O}_4 + 4\text{H}_2\text{S} = 3\text{FeS} + \text{S} + 4\text{H}_2\text{O}$ .

H. Rose, C. F. Plattner, C. F. Rammelsberg, and F. von Schaffgotsch found that all the higher sulphides of iron furnish the monosulphide when heated in hydrogen. K. Friedrich, L. Gedel, G. Ripp, and H. Scheuer also obtained pyrrhotite by heating pyrite; and H. Rose, by heating the pyrite in an atm. of hydrogen. G. Marchal, and B. G. Bredberg observed that when pyrite is melted, it forms ferrous sulphide, or, according to C. F. Rammelsberg, pyrrhotite. The results depend on the duration of the heating; and, according to G. Marchal, and K. Friedrich, with longer periods of heating the product approximates more and more closely to ferrous sulphide. E. Kothny added that at  $700^{\circ}$  with sulphur vapour at one atm. press. the product becomes very nearly ideal ferrous sulphide. E. T. Allen and co-workers emphasized the difficulty in preparing ferrous sulphide of a high degree of purity; and R. Loebe and E. Becker found that ordinary ferrous sulphide always contains free iron, and some oxide; they obtained a product with 98.72 per cent. FeS by repeatedly melting natural pyrites. F. Foreman was unable to prepare satisfactory pyrrhotite. E. T. Allen and co-workers obtained pyrrhotite by the dissociation of pyrite in an atm. of hydrogen sulphide at  $550^{\circ}$ ; at  $575^{\circ}$ , the reverse change occurs, and pyrite is re-formed. E. T. Allen observed that in an atm. of sulphur, pyrite begins to pass into pyrrhotite and sulphur at  $575^{\circ}$ , the reaction is rapid at  $665^{\circ}$ , and at  $750^{\circ}$ , the vap. press. is 1 atm., and decomposition is complete. W. F. de Jong and H. W. V. Willems added that the evolution of sulphur from pyrite is marked at  $525^{\circ}$  to  $550^{\circ}$  in vacuo. Ferrous sulphide is formed when pyrite is reduced by hydrogen as shown by A. Andziol, F. Martin and O. Fuchs, H. Rose, G. Gallo, and L. Wöhler and co-workers; by steam at  $300^{\circ}$  to  $400^{\circ}$ —L. Benedek; by carbon—J. L. Proust; by aluminium as in the thermite process:  $2\text{FeS}_2 + 2\text{Al} = \text{Fe} + \text{Al}_2\text{S}_3$ . FeS—N. Parravano and P. Agostini, H. Ditz, and H. Heinrichs; and by iron—N. G. Petinot. L. Michel

heated titaniferous iron intimately mixed with pyrites in a graphite crucible for several hours, and obtained slightly magnetic pyrrhotite, approximating  $\text{Fe}_9\text{S}_9$ , of sp. gr. 4.5, and hardness 4.

According to F. Stolba, H. Schiff, and E. Glatzel, when anhydrous ferrous or ferric sulphate mixed with sulphur, is heated, ferrous sulphide is formed:  $\text{FeSO}_4 + 2\text{S} = \text{FeS} + 2\text{SO}_2$ , and, added K. Brückner, some iron disulphide may also be formed. H. Rose obtained similar results by heating a mixture of sulphate and sulphur in a current of hydrogen. According to W. Ipatéeff, anhydrous ferrous sulphate at  $330^\circ$  and 200 atm. press., is reduced by hydrogen to ferrous and ferrosic sulphides, and at  $350^\circ$  and 260 atm. press., to ferrous sulphide alone. P. Berthier found that ferrous or ferric sulphate is reduced by carbon to ferrous sulphide; G. P. Schweder, that the reduction with carbon monoxide yields a mixture of ferrous sulphide, oxide, and metal; and H. Heinrichs and C. A. Becker, that the sulphate is reduced to sulphide by powdered magnesium, aluminium, or iron. H. Arcrowsky, J. Durocher, and C. Doelter obtained crystals of troilite by heating ferric chloride in an atmosphere of hydrogen sulphide at  $400^\circ$ . Other sulphides are also formed. C. Doelter heated a mixture of ferrous chloride, sodium carbonate, water, and hydrogen sulphide in a sealed tube for 16 days at  $200^\circ$ , and obtained pyrrhotite when air was excluded, and pyrite when air was present. E. Weinschenk heated a soln. of ferrous chloride with ammonium thiocyanate in a sealed tube at  $230^\circ$  to  $250^\circ$  for 4 hrs., and obtained small, hexagonal plates of ferrous sulphide—J. Milbauer added that some  $\text{K}_2\text{Fe}_2\text{S}_4$  is formed at the same time. E. T. Allen and co-workers repeated the experiment and obtained in every case pyrrhotite or ferrous sulphide associated with free sulphur. J. Meyer and H. Bratke obtained crystals of ferrous sulphide by melting a mixture of iron, sulphur, and potassium cyanide in the proportion 1 : 5 : 5; and J. Morel, by heating to redness a mixture of iron filings and antimony sulphide.

A hydrated form of ferrous sulphide is obtained as a bulky, black precipitate when an alkali sulphide is added to a soln. of a ferrous salt:  $\text{FeCl}_2 + (\text{NH}_4)_2\text{S} = 2\text{NH}_4\text{Cl} + \text{FeS}$ , and if a ferric salt be similarly treated, it is first reduced to ferrous salt and sulphur is simultaneously deposited:  $2\text{FeCl}_3 + 3(\text{NH}_4)_2\text{S} = 6\text{NH}_4\text{Cl} + 2\text{FeS} + \text{S}$ . The reactions were discussed by H. Baubigny, and F. Fouqué and A. Michel-Lévy. According to W. Feld, when soln. of iron salts are treated with an alkali polysulphide, ferrous sulphide and sulphur are precipitated, and if the soln. be then neutralized, or made feebly acidic, and boiled, iron disulphide is formed. Alkaline substances retard or hasten the transformation, while reducing agents accelerate the change. On the other hand, H. N. Stokes stated that the precipitate which is formed when alkali sulphides are added to soln. of ferric salts is not a mixture of ferrous sulphide and sulphur, but rather ferric sulphide; and that ferric sulphide is the product of the action of alkali polysulphides on soln. of ferrous salts. The precipitation with ammonium polysulphide was studied by G. Buchner, E. Jordis and E. Schweizer, A. B. Macallum, H. Krepelka and W. Podrouzek, W. Mecklenberg and V. Rodt, P. P. Budnikoff and K. E. Krause, and A. Wiener. J. J. Berzelius said that hydrated ferric sulphide is formed if an aq. soln. of a ferric salt be dropped into an excess of an alkali sulphide soln.; but if, on the contrary, the alkali sulphide be dropped into an excess of ferric salt, sulphur is first precipitated, and a ferrous salt is formed, whilst further additions of the alkali sulphide furnish a precipitate of ferrous sulphide. L. Gedel said that if the mixture of ferrous sulphide and sulphur be dried above  $100^\circ$ , some iron disulphide is formed:  $3\text{FeS} + \text{S} = \text{FeS}_2 + 2\text{FeS}$ . The reaction of hydrogen sulphide, etc., on ferric salt soln. was studied by O. Brunck, L. Gedel, O. W. Gibbs, H. Krepelka and W. Podrouzek, and R. Scheuer. According to L. L. de Koninck, sodium sulphide gives a brown to green coloration with ferrous or ferric salts. The best condition for the green coloration is 320 to 800 mols of sodium sulphide to one gram-atom of iron. The production of the green coloration is retarded by the presence of sodium chloride or sulphate. The subject was studied by G. W. A. Foster.

The action of hydrogen sulphide on soln. of ferrous salts is reversible,  $\text{FeSO}_4 \rightleftharpoons \text{H}_2\text{S} \rightleftharpoons \text{H}_2\text{SO}_4 + \text{FeS}$ ; consequently, ferrous sulphide is not precipitated by the action of hydrogen sulphide on acidic soln. The subject was discussed 10. 57, 9. In the language of the ionic theory, the precipitation of ferrous sulphide:  $\text{Fe}^{++} + \text{S}'' = \text{FeS}_{\text{solid}}$  is determined by the product  $[\text{Fe}^{++}][\text{S}''] = \text{constant}$ , which is very small. To ensure the precipitation of all the iron, the concentration of  $\text{S}''$ -ions should be proportionally large. Again, in the ionization of hydrogen sulphide,  $\text{H}_2\text{S} \rightleftharpoons \text{H} + \text{HS}' \rightleftharpoons 2\text{H}^+ + \text{S}''$ , in sat. soln.  $[\text{H}]^2[\text{S}''] = K'[\text{H}_2\text{S}]$ , where  $K'$  is constant. Hence, the greater the concentration of the  $\text{H}^+$ -ions, *i.e.* the greater the acidity of the soln., the smaller is that of the  $\text{S}''$ -ions. Hence, ferrous sulphide is not precipitated by hydrogen sulphide in acidic soln. The precipitation of ferrous sulphide by hydrogen sulphide is incomplete even in neutral soln., for, as shown by L. L. de Koninck, the supernatant liquor, at the end of the reaction, is green. The presence of sodium acetate in neutral soln. favours the precipitation of ferrous sulphide because the acetate-ions from the sodium acetate unite with the  $\text{H}^+$ -ions to form acetic acid, and this reduces the conc. of the  $\text{H}^+$ -ions. Hence, as shown by J. L. Gay Lussac, H. Vestner, L. Moser and M. Behr, R. F. Weinland, H. Rose, F. Strohmeier, C. C. Grischow, H. W. F. Wackenroder, and R. Winderlich, ferrous sulphide may be precipitated from soln. containing a weak acid—*e.g.* carbonic, benzoic, oxalic, tartaric, acetic, citric, and succinic acids. H. Dellfs said that no precipitation occurs with formic acid.

The equilibrium constant  $K$  of the reaction  $\text{FeS} + 2\text{H}^+ \rightleftharpoons \text{Fe}^{++} + \text{H}_2\text{S}$  is  $[\text{Fe}^{++}][\text{H}_2\text{S}] = K[\text{H}^+]^2$ ; and the constant  $k$ , or the solubility product for the reaction  $\text{FeS} \rightleftharpoons \text{Fe}^{++} + \text{S}''$  is  $k = [\text{Fe}^{++}][\text{S}'']$ , so that  $[\text{Fe}^{++}] = k/[\text{S}'']$ . Again, for the reaction  $\text{H}_2\text{S} \rightleftharpoons \text{H} + \text{HS}'$ ,  $\text{H}_2\text{S} = [\text{H}][\text{HS}']/k$ , where, according to F. Auerbach, and J. Knox,  $k_1 = 0.91 \times 10^{-7}$ ; and for the reaction  $\text{HS}' \rightleftharpoons \text{H}^+ + \text{S}''$ ,  $[\text{H}^+] = k_2[\text{HS}']/[\text{S}'']$ , where  $k_2 = 1.2 \times 10^{-15}$ . Consequently,  $K = k/k_1k_2$ . L. Bruner and J. Zawadsky found that  $k = 3.7 \times 10^{-19}$ , so that  $K = 3.4 \times 10^3$ .

H. Vestner observed that if  $N\text{-FeSO}_4$  be sat. with hydrogen sulphide at ordinary temp., and heated under press. at  $100^\circ$ , ferrous sulphide is not precipitated quantitatively, but if ammonium acetate be present, the precipitation is quantitative from soln. by not more than 1.0 grm. of ferrous sulphate per litre; and with neutral 0.001*N*- and 0.0001*N*-soln. of ferrous sulphate, at ordinary press., no precipitation occurs at all. G. Bruni and M. Padoa observed that conc. soln. of ferrous salts, acidified with hydrochloric acid, give a precipitate of ferrous sulphide when treated with hydrogen sulphide at 14.34 to 16.38 atm. press., and at  $10^\circ$  to  $15^\circ$ . From the equilibrium:  $\text{FeSO}_4 + \text{H}_2\text{S} \rightleftharpoons \text{FeS} + \text{H}_2\text{SO}_4$ , or  $\text{Fe}^{++} + \text{H}_2\text{S} \rightleftharpoons 2\text{H}^+ + \text{FeS}$ , it follows that the equilibrium constant  $K = [\text{Fe}^{++}][\text{H}_2\text{S}]/[\text{H}^+]^2$ . By increasing the press., the solubility of hydrogen sulphide in the soln. is augmented, and the conc. of the  $\text{Fe}^{++}$ -ions in soln. is reduced to maintain the constancy of  $K$ . This was proved by M. Padoa and L. Cambi. They found the press. at which ferrous sulphide is precipitated from soln. with a mol of ferrous sulphate per litre, at  $22^\circ$ :

$\text{H}_2\text{SO}_4$	—	0.002	0.0025	0.003	0.005	0.001 mol per litre
$\text{H}_2\text{S}(\text{about})$	0.3	0.98	2.7	4.0	5.5	9.2 atm.
$\text{H}_2\text{S}$	—	0.098	0.27	0.40	0.55	0.92 mol per litre
$K$	—	$10.6 \times 10^3$	$10.7 \times 10^3$	$9.7 \times 10^3$	$3.5 \times 10^3$	$2.3 \times 10^3$

W. Böttger, and R. C. Wells discussed the precipitation of ferrous and copper sulphides from a mixed soln. of copper and ferrous salts; L. Storch studied the joint precipitation of stannous and ferrous sulphides from acid soln. of mixed ferrous and stannous salts; W. Feld, mixed ferrous and zinc salts; E. Schürmann, and F. Feigl, mixed ferrous, zinc, cobalt, and nickel salts; and C. A. O. Rosell, mixed ferric and manganese salts. W. Feld found that ferrous sulphide is quantitatively precipitated by passing hydrogen sulphide into a neutral soln. of a ferrous salt containing an excess of sodium thiosulphate; and the reaction was studied by O. W. Gibbs, and O. Brunck. The precipitation of ferrous sulphide from a soln. of ferrous sulphite by hydrogen sulphide was studied by W. Feld, and

H. W. Hemingway. The anodic separation of sulphide films was studied by E. Beutel and A. Kutzelnigg.

According to S. Veil, ferric oxide prepared by heating iron sulphide obtained by precipitating a ferrous or ferric salt with ammonium sulphide, and afterwards treated with hot water, is more magnetic than the corresponding oxide derived from iron sulphide prepared in the cold. The sulphides show the same difference, the former being most stable to oxidation, and the latter having a magnetization of the same order as that of its corresponding oxide. On redissolving the oxide and reprecipitating the sulphide successively, the magnetizations of both rise to a maximum and then fall.

Black, voluminous **hydrated ferrous sulphide** is precipitated when an alkali sulphide is added to a soln. of a ferrous salt:  $\text{FeCl}_2 + (\text{NH}_4)_2\text{S} = \text{FeS} + 2\text{NH}_4\text{Cl}$ ; and if a ferric salt is used it is first reduced to the ferrous state:  $2\text{FeCl}_3 + 3(\text{NH}_4)_2\text{S} = 2\text{FeS} + 6\text{NH}_4\text{Cl} + \text{S}$ . As indicated above, ferric sulphide may first be precipitated, and, as indicated below, if an excess of the precipitant is used, sulphoferrites may be formed. The product of the action of moist iron on sulphur—*vide supra*, the action of iron on sulphur—discussed by L. N. Vauquelin<sup>8</sup>—is considered to furnish the hydrated sulphide. The green soln. obtained by the action of iron-filings on water sat. with hydrogen sulphide for 24 hrs., out of contact with air, is supposed by L. N. Vauquelin to be a soln. of hydrated ferrous sulphide; and O. Henry regarded the green soln. obtained by adding calcium sulphide to a soln. of ferrous sulphate as a soln. of the sulphide. The dark green soln. obtained by the action of water on the precipitated hydrate was also considered to show that the compound is soluble in water. More probably it is a case of the peptization of a colloid. J. J. Berzelius found that heat, and the addition of ammonium hydrosulphide or hydrogen sulphide precipitates the sulphide from the green soln. Precipitated ferrous sulphide, like many other hydrogels, may be partially peptized when it is washed, forming a green hydrosol; and J. C. Witt, and A. Berg even noted that the fused sulphide may be partially peptized when it is treated with water. S. M. Kuzmenko found that with mixed soln. of manganese and ferrous sulphates or gelatin, the more soluble sulphide is precipitated first by sodium sulphide.

L. T. Wright prepared a **colloidal solution of ferrous sulphide** by digesting precipitated ferrous sulphide with a soln. of potassium cyanide, and C. Winssinger, by treating ferrous salt with hydrogen sulphide in soln. so dil. that all extraneous compounds can be removed by dialysis before coagulation occurs. L. Sabbatani, J. Hausmann, and S. M. Kuzmenko obtained the colloid by treating a soln. of ferrous sulphate and gelatin with sodium sulphide, but not with ammonium sulphide; J. Lefort and P. Thibault used gum arabic as protective colloid; A. Dumansky and A. Buntin, tartaric acid; H. Rose, organic substances, particularly tartaric acid; A. Müller, glycerol; and L. Sabbatani, cane-sugar. R. E. Stevens obtained it by the action of sodium hydroxide, as peptizing agent, on ferrous sulphide; and C. L. Sagui and A. Jourdan, by the action of sodium sulphide on the metal sulphide. The hydrolysis of the colloid was noted by H. Rose, and A. Kanschegg and H. Malfatti; J. C. Witt found that when the hydrosol is dialyzed through collodion, some sulphur hydrosol, and iron oxide are formed. S. M. Horsch obtained a hydrosol so concentrated that it set to a jelly when cooled to 0°. When air is passed through the green hydrosol, J. C. Witt observed that the green colour changes to brown. P. B. Ganguly and N. R. Dhar observed that the hydrosol is coagulated and oxidized completely by 15 hrs'. exposure to tropical sunlight. T. Pinter, and J. Casares studied the colloid. J. H. L. Vogt, and R. Lorenz and W. Eitel observed that ferrous sulphide may form a **pyrosol** in molten silicates. R. F. Weinland found that a soln. of ferric acetate forms a dark green hydrosol when it is treated with ammonium sulphide. N. R. Dhar and A. C. Chatterji observed that the hydrosol is adsorbed by freshly-precipitated ferrous sulphide.

H. Braconnot said that the black mud which collects at the bottom of drains

contains hydrated ferrous sulphide formed by the putrefaction of organic substances in contact with the ferric oxide of the earthy matters. M. Sidorenko called the hydrated ferrous sulphide,  $\text{FeS} \cdot n\text{H}_2\text{O}$ , which occurs in numerous clays, **hydro-troilite**. According to B. Doss, it is a complex hydroxide. J. Habermann found it in clays; N. Andrussoff, in the mud of the Black Sea; M. Jegunoff, in the mud of the Sea of Azov, and some saline springs; and A. Jentsch, in the mud of the Lake of Plön. The nature of this mineral was discussed by P. Tschirvinsky, and C. L. Sagui and A. Jourdan.

**The physical properties of ferrous sulphide and pyrrhotite.**—According to L. Gedel,<sup>9</sup> and R. Scheuer, the colour of powdered ferrous sulphide is greyish-green, and, owing to oxidation, reddish specks of oxide soon appear in the powder. E. Weinschenk, E. T. Allen and co-workers, and R. Lorenz and P. Groth observed that when prepared in a dry way, ferrous sulphide is a brass-yellow crystalline mass which in time darkens and becomes reddish-brown. The colour of pyrrhotite varies from a bronze-yellow to a copper-red, and the lustre is metallic, but the surface soon tarnishes on exposure to air. The streak is greyish-black. E. T. Allen and co-workers found that the colour of synthetic pyrrhotite resembles that of the natural mineral, but when prepared from sulphur and iron, the colour is a little darker than that of the natural mineral. M. Bamberger and R. Grengg observed no change in the colour of the mineral when it is cooled down to  $-190^\circ$ ; J. A. Hedvall discussed the colour changes which occur on heating ferrous sulphide.

A. Streng suggested that the **crystals** of pyrrhotite are rhombic and isomorphous with sternbergite, but later concluded that they are hexagonal. The measurements of J. Roth, W. Nicol, K. Vrba, A. Frenzel, and P. A. von Sachsen-Coburg correspond with crystals belonging to the rhombic system; and P. Weiss concluded that the magnetic properties of pyrrhotite indicate that the crystals are probably monoclinic, but do not possess a higher symmetry than rhombic; and E. Kaiser said that the magnetic and other properties show that the mineral occurs in twinned rhombic crystals. J. Morel, and G. Linck thought the crystals were cubic, but this is a mistake. E. Weinschenk reported that the crystals of ferrous sulphide are bronze-yellow, hexagonal plates; and R. Lorenz and P. Groth, and C. Doelter described them as silver-white plates which rapidly tarnish in air. G. Rose measured the axial ratio, and found  $a:c=1:0.8701$ ; E. T. Allen and co-workers gave  $1:0.8632$  to  $0.8742$ ; and P. Groth and K. Mieleitner recalculated G. Rose's data, and gave  $1:1.7402$ . E. T. Allen and co-workers found that the crystals of troilite and of pyrrhotite are identical. Pyrrhotite usually occurs massive, with a granular structure. Distinct crystals are rare; they are generally tabular, and also acute pyramidal with their faces striated horizontally. C. Doelter observed that the crystals of pyrrhotite prepared in the wet way usually occur in plates, whilst when prepared in the dry way, they furnish columns or needles. L. Bucca obtained isolated crystals, and tabular, iridescent crystals arranged in rosettes. According to J. B. L. Romé de l'Isle, J. F. L. Hausmann, C. C. Leonhard, and J. L. de Bournon, the crystals of pyrrhotite are hexagonal. G. A. Kenngott gave for the axial ratio  $a:c=1:1.72315$ ; W. Nicol,  $1:1.419$ ; and A. Streng,  $1:1.165022$ . The hexagonal crystals were described by A. d'Achiardi, J. Beckenkamp, L. Bombicci, A. Breithaupt, L. Bucca, K. Busz, E. S. Dana, C. Doelter, H. Ehrenberg, K. Honda and J. Okubo, E. Kaiser, A. Lacroix, H. Miers, O. Mügge, W. Nicol, G. vom Rath, F. Sandberger, G. Seligmann, C. U. Shepard, J. S. Stevenson, G. Hägg and I. Sucksdorff, and A. Streng. Pyrrhotite, however, also occurs in a rhombic form with the axial ratios, according to E. T. Allen and co-workers, ranging from  $a:b:c=0.5793:1:0.9267$  to  $0.5793:1:0.9927$ . H. Heritsch gave  $a:b:c=1.170:1:0.778$ , and  $2V=67^\circ 58'$ .

N. Alsén said that the X-radiograms of hexagonal pyrrhotite correspond with a lattice having the parameters  $a=3.43 \text{ \AA}$ , and  $c=5.68 \text{ \AA}$ , or  $a:c=1:1.66$ , with  $2\text{FeS}$  mols. in each elementary parallelepiped; concordant data were also reported by W. F. de Jong, P. F. Kerr, W. F. de Jong and H. W. V. Willems,

A. Michel and G. Chaudron, and C. Fontana. N. Alsén observed that a sample of sulphide prepared by adding ammonium sulphide to a soln. of ferrous sulphate, or by the action of moisture on a mixture of iron and sulphur, and then heated half an hour in hydrogen sulphide, had the pyrrhotite structure, and after heating to dull redness, the pyrite structure. Above  $200^{\circ}$ , A. Michel and G. Chaudron found that pyrrhotite rapidly passes into a ferromagnetic variety with  $a=3.47$  Å., and  $c=5.72$  Å., and at  $450^{\circ}$ , this reverts to a metastable variety with  $a=3.40$  Å., and  $c=5.70$  Å. Precipitated ferrous sulphide behaves similarly, except that above  $480^{\circ}$  it passes irreversibly into a non-magnetic variety with  $a=3.36$  Å., and  $c=5.65$  Å.

According to C. Fontana, the interaction of magnetite and hydrogen sulphide, under atm. press. at  $1000^{\circ}$ , does not furnish  $\text{Fe}_3\text{S}_4$ , as supposed by T. Sidot and C. Friedel, but rather is the reaction symbolized:  $\text{Fe}_2\text{O}_3 \cdot \text{FeO} + 4\text{H}_2\text{S} = 3\text{FeS} + \text{S} + 4\text{H}_2\text{O}$ . The sulphur does not occupy a fixed, characteristic position in the crystal-lattice, and the existence of  $\text{Fe}_3\text{S}_4$  as a chemical individual has not been proved. The lattice constants of troilite are  $a=3.43$  Å.,  $c=5.79$  Å., or  $a:c=1:1.686$ , while for natural and artificial pyrrhotite they are virtually the same,  $a=3.43$  Å.,  $c=5.68$  Å., or  $a:c=1:1.666$ . F. Heide and co-workers gave  $a=3.439$  Å., and  $c=5.855$  Å. for hexagonal troilite. J. W. Gruner pointed out that the S-atoms alone have the positions for hexagonal close-packing; the axial ratio  $a:c=1:1.688$  shows that

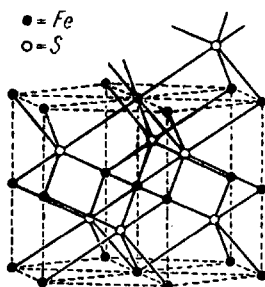


FIG. 606.—The Space-Lattice Structure of Pyrrhotite.

the packing is not so close as for wurtzite for which  $a:c=1:1.633$ . The S-atoms form almost regular tetrahedrons which do not contain any metal atoms. Each Fe-atom is surrounded by six S-atoms which are distributed at the corners of a slightly distorted octahedron, Fig. 606. No structural reason for the easy replacement of iron by sulphur atoms has been observed unless it be the tendency for the S-atoms to form S-S-radicles as in pyrite. In pyrrhotite, the replacement of Fe-atoms by S-atoms would bring the S-atoms as close as 2.45 Å., whilst in the pyrrhotite-lattice they are separated by at least 3.43 Å. P. P. Ewald and G. Hermann added that the lattice of hexagonal pyrrhotite belongs to the nicolite type, with six neighbouring atoms at a distance of 2.55 Å. apart. O. Stelling, and V. M. Goldschmidt also discussed the replacement of the atoms of iron in the space-lattice by atoms of sulphur, and inferred that the lattice in consequence is not ionic. The subject was discussed by A. Westgren, G. Hägg and co-workers, and R. Juza and W. Biltz.

W. Orloff said that the crystals of ferrous sulphide are isomorphous with wurtzite,  $\text{ZnS}$ , greenockite,  $\text{CdS}$ , and millerite,  $\text{NiS}$ . A. Breithaupt discussed the isomorphism of pyrrhotite and iridosmine, niccolite, greenockite, millerite, and breithauptite; G. A. Kennigott, with millerite; F. von Kobell, with niccolite; and C. Doelter, with wurtzite. **Twinning** occurs with pyrrhotite about the  $(10\bar{1}1)$ -plane with the vertical axes nearly at right angles. The **cleavage** (0001) is sometimes distinct, and the  $(11\bar{2}0)$ -parting less so. A. Streng found that the **corrosion figures** of pyrrhotite with hot hydrochloric acid correspond with hexagonal symmetry. The optical properties of polished surfaces were discussed by J. Murdoch, W. M. Davy, and C. M. Farnham, H. Schneiderhöhn, and B. Granigg. M. Leo, H. C. Boydell, and J. Lemberg discussed the behaviour of polished surfaces with various reagents—nitric, hydrochloric, and sulphuric acids, bromine water, potassium cyanide, potassium hydroxide, and a soln. of copper sulphate, mercuric chloride, and ferric chloride; and J. W. Gruner, and W. H. Newhouse, intergrowths of pyrrhotite crystals. M. J. Buerger studied the deformation of the crystals by pressure.

E. T. Allen and co-workers showed that the crystal constants of pyrrhotite are not invariable because the composition, even of artificial preparations, is not con-

stant. The lack of agreement amongst the crystallographers, indicated above, as to the crystal system of pyrrhotite is explained by the existence of two **allotropic forms**. The ordinary hexagonal form, called  **$\beta$ -pyrrhotite**, is stable below about  $138^\circ$ ; and the high temp. form,  **$\alpha$ -pyrrhotite**, is stable above that temp., and it furnishes rhombic crystals with the axial ratios indicated above. If hydrogen sulphide is allowed to act on an acidic soln. of ferrous chloride and sulphate at  $200^\circ$  to  $225^\circ$ , tabular, twinned crystals of  $\alpha$ -pyrrhotite are formed; and the crystals of  $\beta$ -pyrrhotite are produced when a soln. of ferrous sulphate, sat. with hydrogen sulphide at  $0^\circ$ , is heated in a sealed tube between  $80^\circ$  and  $100^\circ$  for 8 days. The habit of the artificial crystals of the  $\beta$ -variety is hexagonal, and the dominant forms are the prism, and a steep pyramid, whilst the crystals of the  $\alpha$ -variety are always tabular, parallel to the base—a few are hexagonal but they are mostly elongated in the direction of the  $\alpha$ -axis, and the symmetry is rhombic. The low temp., or  $\beta$ -form, is almost invariably developed as cruciform twins with an angle of about  $90^\circ$  between the two individuals about the twinning ( $10\bar{1}1$ )-plane; whilst the high temp. or  $\alpha$ -form is usually twinned about the (023)-plane, with the two individuals inclined about  $65^\circ$  to each other; sometimes the twinning is about the (021)-plane; with the two individuals inclined about  $55^\circ$  to each other—*vide supra*.

H. le Chatelier and A. Ziegler noted that the heating curve of ferrous sulphide indicates that there is a **transition temperature** at about  $130^\circ$ ; this was confirmed by W. Treitschke and G. Tammann. R. Loebe and E. Becker, and E. Becker placed it at about  $138^\circ$ . G. Tammann and R. Kohlhaas studied the effect of press. on the transition. F. Rinne and H. E. Boeke observed that two specimens of ferrous sulphide occurring in meteoric iron show the same transition, no break in the cooling curve occurs with a third natural specimen or with a sulphide prepared by heating the elements together without access of air. When the sulphide last mentioned has been fused previously with excess of iron, however, it showed the transition point. When 7 per cent. of iron or more was present, the change took place sharply at  $137^\circ$ , but with less iron it was not so sharp and occurred at lower temperatures; with less than 4 per cent. the break in the cooling curve could no longer be detected. It is, therefore, considered that iron and the sulphide form mixed crystals at  $138^\circ$  which are sat. at 7 per cent. of iron and are readily transformed into another modification. The way in which iron facilitates the transformation has not been elucidated satisfactorily. The fact that the transformation takes place so sharply in troilite, which does not contain excess of iron, is accounted for by the catalytic action of a small proportion of carbon it contains. K. Friedrich, and E. T. Allen and co-workers confirmed these results, and stated that the failure to observe dissolved iron, must mean that the heat absorption in them is so very gradual that its effect is not shown on the heating curve. R. Loebe and E. Becker found that there is a critical temp. on the heating and cooling curve at  $298^\circ$ ; P. Chevenard, one on the thermal expansion curve at  $320^\circ$ ; and H. le Chatelier and A. Ziegler, one on the thermal and expansion curves at  $298^\circ$ . The subject was discussed by R. Lorenz and W. Herz.

L. Playfair and J. P. Joule <sup>10</sup> gave 5.035 for the mean **specific gravity** of artificial ferrous sulphide; C. F. Rammelsberg gave 4.79 for a sample derived from iron and sulphur, and 4.694 for a sample reduced from pyrite in hydrogen; G. Rose, 4.726 at  $9.8^\circ$  for a sample reduced from pyrite in hydrogen; and E. T. Allen and co-workers, 4.739 at  $25^\circ/4^\circ$  for a sample derived from iron and sulphur at  $950^\circ$ , and 4.748 at  $25^\circ/4^\circ$  for a sample prepared at  $950^\circ$  using more sulphur. N. Alsén calculated 5.02 for the sp. gr. from the lattice constants, and W. F. de Jong and H. W. V. Willems, 5.01. G. Luck gave 4.52 for the sp. gr. of troilite; C. F. Rammelsberg, 4.817 for a sample with 1.55 to 1.95 per cent. of nickel, 4.75 for a sample with 0.32 per cent. of nickel, and 4.787 for a sample with no nickel; W. J. Taylor gave 4.822 for a sample with 7.26 per cent. of nickel and cobalt; E. Cohen, 4.7379 at  $22^\circ$  for a sample with 4.30 and 1.50 per cent. of nickel and cobalt respectively;



J. L. Smith, 4.75; F. E. Geinitz, 3.98; and S. Meunier, 4.780 to 4.799. The sp. gr. of pyrrhotite was reported by C. F. Rammelsberg to be 4.640; G. A. Kenn-gott gave 4.584; A. d'Achiardi, 4.53; A. Hilger, 4.12 to 4.20; T. Petersen, 4.583; F. von Schaffgotsch, 4.546; J. Thiel, 4.508; G. Lindström, 4.627 to 4.642; G. Nyiredy, 4.5; M. Tournaire, 4.27; J. J. Berzelius, 4.674; C. F. Plattner, 4.627; H. Heritsch, 4.63; P. Berthier, 4.80; and B. J. Harrington, 4.622. Observations were also made by C. Hatchett, H. Habermehl, A. Frenzel, A. A. Julien, M. Palfy, P. Weiss, E. Manasse, A. Serra, W. J. Sharwood, and F. Stutzer and co-workers. C. F. Rammelsberg gave for artificial pyrrhotite (36 per cent. of sulphur), 4.494; C. Doelter, 4.521 for  $\text{Fe}_{11}\text{S}_{12}$ ; L. Bucca, 4.545 for  $\text{Fe}_4\text{S}_5$ ; L. Michel, 4.5; E. J. L. Holman, 5.02; and J. B. Peel and co-workers obtained 4.63 for the sp. gr. of the synthetic compound  $\text{FeS}$ ; F. Gieseler, 4.807 at  $25^\circ/4^\circ$ ; and W. Biltz, 4.816. W. F. de Jong and H. W. V. Willems calculated 5.01 for the sp. gr. from the X-radiograms. E. T. Allen and co-workers gave for a series of synthetic pyrrhotites, with different proportions of  $\text{FeS}$ , and of dissolved sulphur, the following values for the sp. gr. at  $25^\circ/4^\circ$ , the calculated sp. gr. at  $4^\circ$ , and the calculated specific volume :

FeS . . .	99.59	98.04	96.89	96.57	96.26	95.86	95.23	93.95 per cent.
Excess . . .	0.41	1.96	3.11	3.43	3.74	4.14	4.77	6.04 . . .
Sp. gr. . . .	4.769	4.691	4.657	4.648	4.633	4.602	4.958	4.533 . . .
Sp. gr. (calc.).	4.755	4.677	4.643	4.634	4.619	4.589	4.585	4.520 . . .
Sp. vol.. . .	0.2103	0.2138	0.2154	0.2158	0.2165	0.2179	0.2181	0.2212 . . .

The locus of the sp. vol. is continuous and a straight line in accord with the hypothesis that the excess sulphur is in solid soln., Fig. 607. The dotted line shows the calculated sp. vol. of the sulphur and ferrous sulphide. There is therefore a large contraction in the process of solution. F. Gieseler gave 18.3 for the mol. vol., and calculated 11.2 for the mol. vol. of the contained sulphur, and 28 per cent. contraction during the formation of the sulphide. W. Biltz, and I. I. Saslawsky also discussed the contraction which occurs in the formation of ferrous sulphide and of pyrrhotite.

Fig. 607.—The Specific Volumes of Artificial Pyrrhotites.

but is less hard than pyrite; it forms a voluminous powder after a short exposure to air. M. J. Buerger, and F. F. Osborne and F. D. Adams studied the **plastic-deformation** of pyrrhotite. E. J. L. Holman gave 494.4 dynes per sq. cm. for the **surface tension** of ferrous sulphide at about  $1176^\circ$ . J. O. Arnold, and H. le Chatelier and A. Ziegler found that ferrous sulphide diffuses in soft steel between  $1000^\circ$  and  $1100^\circ$ ; and the **diffusion** was discussed by E. D. Campbell—*vide supra*, action of sulphur on iron.

H. Fizeau<sup>11</sup> found that the coeff. of **thermal expansion** of pyrrhotite at  $40^\circ$  is  $\alpha=0.00000235$  in the direction of the principal axis, and  $\alpha=0.00003120$  when perpendicular to that axis. H. le Chatelier and A. Ziegler observed that the relative coeff. of linear expansion  $\alpha$  at a temp.  $\theta^\circ$  when the original length at  $100^\circ$  is taken as zero, is :

	120°	190°	240°	265°	400°	650°
$\alpha$ . . . . .	0.09	0.00	-0.06	0.00	0.35	0.85

There is thus an irregularity between  $100^\circ$  and  $200^\circ$  which is connected with the change in the crystalline form as  $\beta$ -pyrrhotite passes into  $\alpha$ -pyrrhotite. This was discussed by W. Treitschke and G. Tammann. The change between  $295^\circ$  and  $300^\circ$  observed by H. le Chatelier and A. Ziegler, was studied by E. Becker, and R. Loebe and E. Becker. According to P. Chévenard, the thermal expansion of pyrrhotite at  $320^\circ$  is discontinuous, and on cooling, there is an increase in the length of the

sample. On re-heating, the transformation appears at the same temp., but on cooling, the expansion is less. The temp.  $320^{\circ}$  is therefore considered to represent an enantiomorphic transformation. This temp. also corresponds with a change in the magnetization of the compound. C. H. Lees found the **thermal conductivity** of ferrous sulphide to be 0.017 cal. per cm. per degree per second at  $15^{\circ}$ . According to A. Streng, and M. Leo, the thermal conductivity of pyrrhotite shows the circular basis characteristic of the hexagonal system; and E. Jannetaz found that the sq. root of the ratio of the conductivities parallel and perpendicular to the principal axis is 1.07.

H. V. Regnault found the mean **specific heat**,  $c$ , of artificial ferrous sulphide at  $16.57^{\circ}$  to be  $c=0.1357$ ; A. de la Rive and F. Marcet gave  $c=0.1396$  between  $5^{\circ}$  and  $15^{\circ}$ ; and A. Sella, 0.1370. K. Bornemann and O. Hengstenberg found the value of  $c$  between  $0^{\circ}$  and  $\theta^{\circ}$  to be:

	$100^{\circ}$	$300^{\circ}$	$400^{\circ}$	$500^{\circ}$	$600^{\circ}$	$700^{\circ}$
$c$	0.1664	0.2027	0.1888	0.1850	0.1820	0.1813
	$800^{\circ}$	$900^{\circ}$	$1000^{\circ}$	$1100^{\circ}$	$1200^{\circ}$	
$c$	0.1760	0.1757	0.1760	0.1773	0.2216	

The results, plotted in Fig. 608, show that there is an irregularity in the result at about  $300^{\circ}$ , and the transformation is not wholly reversible. The anomaly diminishes with a rise of temp. C. T. Anderson obtained a continuous curve for the mol. ht.,  $C_p$ , below  $25^{\circ}$ :

	$-215.1^{\circ}$	$-198.5^{\circ}$	$-153.1^{\circ}$	$-84.8^{\circ}$	$-51.8^{\circ}$	$-28.4^{\circ}$	$2.8^{\circ}$	$23^{\circ}$
$C_p$	3.729	5.118	8.395	11.07	11.78	12.07	12.79	13.12

A. Sella, K. Jellinek and J. Zakowsky, and J. Maydell discussed the application of the addition rule—1. 13, 13—to the **molecular heat**. F. E. Neumann gave 0.1533 for the sp. ht. of pyrrhotite; H. V. Regnault, 0.16021 between  $9.53^{\circ}$  and  $99^{\circ}$ ; A. Abt, 0.15388 at  $13.40^{\circ}$  for a specimen with 57.68, Fe; 37.66, S; and 4.42,  $\text{SiO}_2$ ; and K. Bornemann and O. Hengstenberg, 0.1547 between  $0^{\circ}$  and  $100^{\circ}$  for a specimen with 57.30, Fe; 37.7, S; and 4.75,  $\text{SiO}_2$ ; and 0.1531 for "pure" pyrrhotite. K. Bornemann and O. Hengstenberg found that between  $0^{\circ}$  and  $100^{\circ}$  the sp. ht. decreased with increasing percentages of sulphur, but not proportionally.

Sulphur	38.0	39.6	40.0	42.5	45.0	47.5	50.0 per cent.
Sp. ht.	0.160	0.152	0.151	0.143	0.137	0.132	0.130

W. A. Tilden gave 0.1459 for the sp. ht. of  $\text{Fe}_3\text{S}_4$  between  $0^{\circ}$  and  $100^{\circ}$ , and 0.1701 between  $0^{\circ}$  and  $300^{\circ}$ . G. Linder observed that the mean sp. ht. between  $0^{\circ}$  and  $\theta^{\circ}$  increases markedly with a rise of temp., being 0.1459 at  $100^{\circ}$ ; 0.1558 at  $200^{\circ}$ ; 0.1701 at  $300^{\circ}$ ; and 0.1831 at  $350^{\circ}$ .

K. Bornemann gave  $1194^{\circ}$  for the **melting-point** of ferrous sulphide; K. Bornemann and F. Schreyer,  $1158^{\circ}$ ; C. B. Carpenter and C. R. Hayward,  $1163^{\circ}$ ; E. J. L. Holman,  $980^{\circ}$ ; K. Friedrich,  $1171^{\circ}$ ; R. Loebe and E. Becker, and E. Becker,  $1193^{\circ}$ ; B. Garre, and W. Biltz,  $1197^{\circ}$ ; G. Röhl,  $1188^{\circ}$ ; L. V. Steck and co-workers,  $1174^{\circ}$ ; D. M. Levy,  $1187^{\circ}$ ; P. P. Fedotéeff,  $1177^{\circ}$ ; Z. Shibata,  $1163^{\circ}$ ; E. T. Allen and co-workers,  $1170^{\circ}$  in vacuo; and A. C. Halferdahl,  $1171^{\circ}$ . Very low values were obtained by H. Freeman, H. Weidmann, and H. le Chatelier and A. Ziegler; and the high value,  $1300^{\circ}$ , of W. Treitschke and G. Tammann shows that the sample was impure. E. T. Allen and co-workers observed that sulphur is slowly given off at the m.p. and a product richer in iron, but of a lower m.p., remains; hence, the augmented values in an atm. of hydrogen sulphide, and sulphur. The presence of an excess of sulphur was found by K. Bornemann to raise the m.p. E. T. Allen and co-workers added that pyrrhotite is a solid soln. of

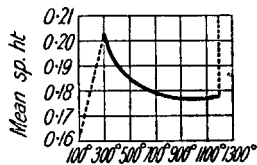


FIG. 608.—The Specific Heat of Ferrous Sulphide.

sulphur in ferrous sulphide, and the m.p. is raised to  $1187^{\circ}$  in an atm. of sulphur vapour; and in an atm. of hydrogen sulphide, at  $1183^{\circ}$ . These temp. correspond with the m.p. of sat. soln. of sulphur in ferrous sulphide. Observations on the subject were made by K. Friedrich. J. H. L. Vogt found that 12.0 grms. of lead sulphide per 100 grms. of ferrous sulphide lowered the m.p.  $31^{\circ}$ ; and 12.4 grms. of silver sulphide lowered it  $38^{\circ}$ . F. Thomas, and H. Freeman examined the effect of sodium sulphide on the m.p.; and K. Bornemann, the effect of lead, nickel, and cuprous sulphides.

R. Lorenz observed no evidence of sublimation when ferrous sulphide is heated to whiteness for a long period of time. K. Jellinek and J. Zakowsky calculated from the equilibrium:  $\text{FeS} + \text{H}_2 \rightleftharpoons \text{Fe} + \text{H}_2\text{S}$ , that the vapour pressure,  $p$ , at  $730^{\circ}$ ,  $910^{\circ}$ , and  $1100^{\circ}$  is respectively  $\log p = -9.15$ ,  $-7.09$ , and  $-4.51$ ; and N. Paravano and P. de Cesaris calculated from the relation  $\log p = -Q/4561T + 1.75 \log T + 3$ , the values 0.079 atm., at  $800^{\circ}$ ; 0.58 atm. at  $900^{\circ}$ ; 3.2 atm. at  $1000^{\circ}$ ; and 13.8 atm. at  $1100^{\circ}$ . K. Bornemann added that the dissociation pressure at the m.p. is perceptible, but much less than an atmosphere; whilst W. Treitschke and G. Tammann obtained a press. approximating one atm. at the m.p. H. le Chatelier and A. Ziegler, R. Juza and co-workers, and M. Picon also discussed the subject. P. Berthier said that when ferrous sulphide is heated white-hot, out of contact with air it loses no sulphur, and when heated similarly in a carbon crucible, it loses weight

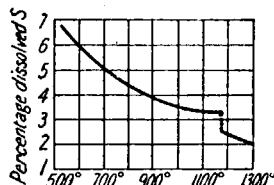


FIG. 609.—The Solubility of Sulphur in Ferrous Sulphide.

very slowly; but J. J. Berzelius observed that sulphur is evolved when ferrous sulphide is heated, and, as indicated above, E. T. Allen and co-workers, as well as W. Treitschke and G. Tammann, and K. Bornemann, found that sulphur is slowly lost at the m.p. R. Kremann and O. Bankovac observed that at  $1500^{\circ}$  molten ferrous sulphide is a mobile liquid, and bubbly. E. V. Britzke and A. F. Kapustinsky gave  $\log p_{\text{S}_2} = -14,329T^{-1} + 5.80$  for the dissociation press. of ferrous sulphide. M. Picon noted that ferrous sulphide dissociates into its elements at a high temp. in vacuo; the dissociation begins at  $1100^{\circ}$ , and is complete at about  $1600^{\circ}$ . If heated in a coke furnace, the resulting iron is carburized, but the carbon exercises no other influence on the dissociation. H. le Chatelier and A. Ziegler, and G. P. Schweder noted the oxidation of the sulphide when it is melted in air. E. T. Allen and co-workers observed that the sulphur dissolved by ferrous sulphide, at atm. press., is:

	600°	800°	1000°	1100°	1165°	1200°	1300°
Dissolved S .	6.04	4.41	3.6	3.3	3.2	2.5	1.96 per cent.

The results are plotted in Fig. 609. When pyrrhotite is cooled in an atm. of nitrogen from:

	1210°	1200°	1000°	900°	800°	700°	600°
Dissolved S .	0.41	0.63	2.70	3.11	3.74	4.14	4.7 per cent.

At  $550^{\circ}$ , pyrrhotite passes into pyrite when heated in an atm. of hydrogen sulphide, and at  $575^{\circ}$ , pyrite begins to change into pyrrhotite, while at about  $565^{\circ}$ , and a press. of about 5 mm. of sulphur vapour, pyrite is in equilibrium with pyrrhotite containing about 6.5 per cent. dissolved sulphur. The reaction is reversible:  $\text{FeS}_2 \rightleftharpoons \text{FeS}(\text{S}_n) + (1-n)\text{S}$ . Troilite, or ferrous sulphide, is the end-member of the series of solid soln. The heating curve of pyrite shows a strong absorption of heat at about  $665^{\circ}$ , indicating that the dissociation is suddenly accelerated, and that the escaping sulphur has a vap. press. of about 1 atm. As previously indicated, L. Gedel found that iron heated with an excess of sulphur to  $450^{\circ}$  or  $500^{\circ}$ , forms iron disulphide; at  $700^{\circ}$ , the product has the composition  $\text{Fe}_7\text{S}_8$ ; and above  $700^{\circ}$ , FeS. According to G. F. Hüttig and P. Lürrmann, the roasting of ferrous sulphide, derived from pyrite, furnishes a curve, Fig. 610, which indicates that

while most of the sulphur is oxidized when the atmosphere contains 16 per cent. of oxygen, and the remainder sulphur dioxide, not quite all the sulphur is expelled even with 100 per cent. of oxygen. This is taken to mean that a solid soln. of sulphur is formed, otherwise, the course of the reaction would correspond with the dotted curve. The dissociation is discussed in more detail in connection with pyrite.

K. Bornemann and O. Hengstenberg found the **heat of fusion** of ferrous sulphide to be 60 cal. per gram. K. Bornemann calculated 31.9 cal. per gram of  $\text{FeS}$ ; and J. H. L. Vogt, 34.4 cal. J. W. Richards also made an estimate based on an empirical formula—**L. 13, 20.**

W. G. Mixter found the **heat of formation** of amorphous ferrous sulphide from rhombic sulphur to be  $(\text{Fe}, \text{S}) = 18.8$  Cals.; N. Parravano and P. de Cesaris, 23.07 Cals.; R. Müllenhoff, 25.0 Cals.; E. Mannheimer, 22.813 Cals.; C. T. Anderson, 23.07 Cals.; E. V. Britzke and A. F. Kapustinsky, 18.0 Cals.; and J. Thomsen, 23.75 Cals.

K. Jellinek and J. Zakowsky gave  $(\text{Fe}, \text{S}) = 39.0$  Cals., and A. C. Halferdahl, 37,825 cal. for gaseous sulphur; and if referred to the  $\text{S}_2$ -molecule, 78.0 Cals. E. V. Britzke and A. F. Kapustinsky gave  $(2\text{Fe}, \text{S}_2) = 65,460$  cal. The value calculated from W. Nernst's formula is 80.6 Cals.; and from J. H. van't Hoff's formula, 62.0 Cals. For the precipitated sulphide, J. Thomsen gave  $(\text{Fe}, \text{S}, \text{Aq.}) = 21.77$  Cals., and M. Berthelot, 24.0 Cals. J. Thomsen gave for the heat of the reaction  $(\text{Fe}(\text{OH})_2, \text{H}_2\text{S}, \text{Aq.}) = 14.7$  Cals.; P. A. Favre and J. T. Silbermann, 18.53 Cals.; and M. Berthelot, 14.6 Cals. J. Thomsen gave for the reaction  $(\text{Fe}(\text{NO}_3)_2, \text{H}_2\text{S}, \text{Aq.}) = -6.7$  Cals. A. C. Halferdahl found the heat of decomposition of pyrite to form a solid soln. of sulphur and ferrous sulphide, is  $-10$  Cals. at  $575^\circ$  to  $680^\circ$ ; he calculated the **free energy** of the reaction  $\text{FeS} + \text{H}_2 = \text{Fe} + \text{H}_2\text{S}$  to be respectively  $-21,170$ ,  $-19,540$ , and  $-17,310$  cal. at  $730^\circ$ ,  $910^\circ$ , and  $1100^\circ$ ; the free energy of ferrous sulphide up to the m.p.,  $1171^\circ$ , is  $-31,820 + 10.49T$ ; and the free energy at  $1171^\circ$  is  $-16,670$  cal. The free energies at  $1200^\circ$ ,  $1300^\circ$ , and  $1400^\circ$  are respectively  $-16,230$ ,  $-14,320$ , and  $-11,850$  cal. From the sp. ht. data of K. Bornemann and O. Hengstenberg, A. C. Halferdahl calculated for the reaction  $\text{Fe} + \frac{1}{2}\text{S}_2 = \text{FeS}$ ,  $Q = -35,360$  cal. before fusion at  $1171^\circ$ . The change of **entropy** before fusion is  $-12.9$  units, and  $-9.7$  units after fusion, so that the entropy of ferrous sulphide is 44.5 units after fusion at  $1171^\circ$ . C. T. Anderson gave  $-23,600$  cal. for the free energy, and 16.1 for the entropy at  $25^\circ$ . K. K. Kelley studied the entropy. G. Beck studied the free energy of the sulphide. E. V. Britzke and A. F. Kapustinsky calculated the free energy or affinity of iron for  $\text{S}_2$ , or  $F = -4.571 \log K_p$ , to be 38,840 cal. at  $996^\circ \text{K.}$ ; 36,830 cal. at  $1073^\circ \text{K.}$ ; 34,360 cal. at  $1170^\circ \text{K.}$ ; and 30,110 cal. at  $1267^\circ \text{K.}$  W. Herz calculated values for the entropy and vibration frequency of  $\text{FeS}$ .

H. Heritsch<sup>12</sup> gave for the **indices of refraction**  $\alpha = 1.686$ ,  $\beta = 1.693$ , and  $\gamma = 1.696$ ; and  $\alpha - \gamma = 0.010$ . A. de Gramont found the **spark spectrum** of pyrrhotite resembled that of pyrite; whilst W. W. Coblentz observed that the **ultra-red reflecting power** of pyrrhotite is higher than that of molybdenite, and increases from about 15 per cent. at  $1.25\mu$  to 48 per cent. at  $14\mu$ . O. Stelling S. Tanaka and G. Okuno, O. Lundquist, and F. Butavand discussed the absorption coeff. for the **X-rays**; and C. Doelter found thin layers of pyrrhotite to be transparent to the X-rays, but not so with thick layers. H. E. J. G. du Bois observed no evidence of the **Kerr effect** with ferrous sulphide; and P. Martin obtained with pyrrhotite,  $\text{Fe}_7\text{S}_8$ , a positive rotation approximating  $1'$  with wavelengths between  $\lambda = 435$  and  $\lambda = 675$ . O. Rohde, and B. Aulenkamp observed that ferrous sulphide exhibits a small **photoelectric effect**, and that the effect with

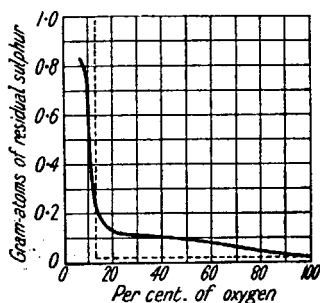


FIG. 610.—Equilibrium in the System:  $\text{Fe-S-O}_2$ .

pyrrhotite comes between that with ferrous sulphide and that with pyrite. Observations were also made by W. Ramsay and J. F. Spencer, and B. Aulenkamp. According to E. T. Wherry, pyrrhotite and troilite are only moderate **radio-detectors**.

W. A. D. Rudge<sup>13</sup> observed that powdered ferrous sulphide in a current of air acquires a positive frictional charge. According to F. Streintz, a rod of compressed powder of ferrous sulphide has a poor **electrical conductivity**; and P. Fischer observed no conductivity at all at 130°. The electrical conductivity of pyrrhotite was measured by M. Faraday, and J. F. L. Hausmann and F. C. Henrici; H. Löwy gave  $2 \times 10^{14}$  c.g.s. units. F. Beijerinck, and R. C. Harvey observed that troilite is a poor conductor, and pyrrhotite a good one, but E. Cohen said that the one conducts as well as the other. J. Guichant, and H. le Chatelier and A. Ziegler observed that artificial ferrous sulphide in the cold is a good conductor. The latter observed that the **electrical resistance** increases five-fold as the temp. rises to 150°; and after that no change occurs until 300° is attained. J. Guichant observed a decrease in the resistance,  $R$  ohms, as the temp. rises to 550°, beyond which there is an increase:

	13°	90°	130°	280°	580°	672°	868°
Heating $R$	0.0998	0.0314	0.00826	0.00125	0.00087	0.00099	0.00171
	868°	670°	580°	249°	130°	95°	8°
Cooling $R$	0.00171	0.00112	0.00099	0.00090	0.00605	0.0273	0.105

Between 0° and 100°,  $R=0.11146(1-0.00798\theta)$ . J. C. McLennan and co-workers found the resistance  $R$  microhms of ferrous sulphide to be 1915 at 27°; 1740 at 0°; 450 at -88°; 73 at -268.8°; and 70 at -271.1°. For the molten sulphide, K. Bornemann and K. Wagenmann gave 0.000684 for the temp. coeff. of the sp. resistance between the m.p. 1194° and 1500°; or

	1194°	1200°	1250°	1300°	1350°	1400°	1500°
$R \times 10^4$	5.862	5.883	6.083	6.284	6.485	6.685	7.087

M. Leo reported that the electrical conductivity of pyrrhotite is different when taken parallel and perpendicular to the principal axis. A. Abt gave for the sp. resistance of a sample from Also Jara,  $R=0.0084$  and  $0.0102$  ohm at 20°. K. Baedeker found that the sp. resistance at 0°, of  $\alpha$ -pyrrhotite parallel to the  $c$ -axis, is  $R=0.00035$ , and vertical to the  $c$ -axis,  $R=0.00035$  ohm; there is a minimum in the resistance curve at about 280°; and J. Königsberger and co-workers observed a minimum at 160° when taken parallel to the  $c$ -axis, and at 200° when taken vertical to that axis. The resistance of a sample of pyrrhotite, approximating FeS, decreases as the temp. rises from -189° to 300°. There is a transition temp. at about 360° corresponding with the change from  $\alpha$ - to  $\beta$ -pyrrhotite, as indicated in Fig. 611, and by the data perpendicular to the  $c$ -axis;

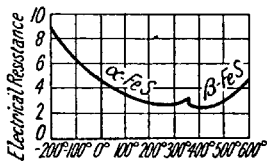


FIG. 611.—The Electrical Resistance of Pyrrhotite at Different Temperatures.

	-189°	-95°	-25°	19°	71°	155°	277°	310°
$R \times 10^4$	8.02	6.60	4.23	4.10	3.70	3.25	2.56	2.62 ohms

Between 350° and 360° there is the transition point, or the Curie point. The resistance of the magnetic and non-magnetic forms are the same at 360°; at 417°,  $R \times 10^4=2.5$  ohms, and at 463°, 2.5 ohms. When taken parallel to the  $c$ -axis, the resistance is:

	-188°	-73°	18°	67°	200°	235°	300°	350°
$R \times 10^4$	10.70	6.45	5.35	5.08	4.25	4.05	3.95	3.87 ohms

The transformation here occurs at 350°. In the vicinity of the transformation point, 350°, 400°, and 445°,  $R \times 10^4=380$ , 380, and 375 respectively. Observations

were also made by F. Streintz and co-workers. F. Streintz and A. Wellik found that the resistance of pyrrhotite, with increasing load, decreases until 2020 grms. when it remains constant with an alternating current; with a direct current, the load is 3000 grms. T. W. Case observed no change in the electrical resistance of pyrrhotite on exposure to light; and P. Fischer studied the conductivity of mixtures of iron sulphide with the sulphides of silver, and of lead. K. Miyazaki found that the electrical resistance of a soln. of ferrous sulphide in iron, at ordinary temp., can be represented by the curve Fig. 612, and that this agrees with the assumption that the solubility of ferrous sulphide in iron at these temp. is very small.

E. V. Britzke and A. F. Kapustinsky<sup>14</sup> gave  $-0.43$  volt for the **electrode potential** of ferrous sulphide. T. J. Seebeck, W. G. Hankel, W. Flight, and A. Abt placed pyrrhotite between iron and antimony in the thermoelectric series. J. Weiss and J. Königsberger found that with a couple of copper and pyrrhotite, the **thermoelectric force** is  $0.000023$  volt between  $20^\circ$  and  $80^\circ$ , and the current

flows from the copper to the pyrrhotite at the hot junction. A rod of ferrous sulphide cut parallel to the  $c$ -axis gives a thermoelectric force of  $0.000026$  volt. A. M. Iljef observed that with a rod of compressed ferrous sulphide, between copper electrodes, a thermoelectric current flows in the direction of the fall of temp. The subject was discussed by K. Baedeker, and A. Travers and J. Aubert.

W. Skey<sup>15</sup> gave for the **electrochemical series** in sea-water:  $-\text{FeS}$ ,  $\text{MnS}$ ,  $\text{ZnS}$ ,  $\text{SnS}_2$ ,  $\text{HgS}$ ,  $\text{Ag}_2\text{S}$ ,  $\text{PbS}$ ,  $\text{Cu}_2\text{S}$ ,  $\text{FeS}_2$ ,  $\text{Sb}_2\text{S}_3^+$ . R. C. Wells found the **electrode potential** of pyrrhotite in  $N\text{-KCl}$  to be  $0.56$  volt, and in  $N\text{-Na}_2\text{S}$ ,  $-0.17$  volt, at  $25^\circ$ —*vide infra*, pyrite—and A. Travers and J. Aubert, the electrode potential of cathodic ferrous sulphide against iron in soln. of sodium sulphate, and of potassium dichromate. R. Zuppinger studied the **electromotive force** of cells of the type  $\text{FeS} | \text{FeSO}_4(\text{or NaHS}) / \text{Na}_2\text{SO}_4 | \text{S} : \text{SO}_4 | \text{Zn}$ . A. Lipschitz and R. von Hasslinger observed that purified ferrous sulphide is passive towards dil. acids, and it is active when metallic iron is present. When measured against a normal calomel electrode, in a soln. of ferrous sulphate and sulphuric acid sat. with hydrogen sulphide, active ferrous sulphide has an e.m.f. of  $-0.03$  volt, which is the same as the e.m.f. of iron; in a soln. of ferrous sulphate in sulphuric acid, passive ferrous sulphide has an e.m.f. of  $+0.90$  volt which is similar to the e.m.f. of pyrite,  $0.89$  volt, marcasite,  $0.89$  volt, and pyrrhotite,  $0.71$  volt; with the same soln., iron has an e.m.f. of  $-0.03$  volt. G. Tammann found the e.m.f. of a cell with pyrrhotite against  $4N\text{-ZnSO}_4$  and zinc is  $1.07$  volts; against a sat. soln. of lead chloride and lead,  $0.53$  volt; against  $2N\text{-CuSO}_4$  and copper,  $0.19$  volt; and against a sat. soln. of silver sulphate and silver,  $0.03$  volt. G. Trümpler found the e.m.f. of a cell with a ferrous sulphide electrode against  $2N\text{-Na}_2\text{S}$  sat. with sulphur, and a calomel electrode, at  $15^\circ$  to  $18^\circ$ , to be  $0.667$  volt; similar results were observed with electrodes of platinum, galena, and cupric sulphide. E. F. Law studied the potential difference between iron and ferrous sulphide. K. Fischbeck found that ferrous sulphide is not reduced when used as cathode in 2 per cent. sulphuric acid at  $20^\circ$ . M. Padoa and B. Zanella observed that in the electrolysis of a soln. of ammonium chloride with an anode of pyrrhotite, the iron passes into soln. in the ferric state. R. C. Wells studied the anodic and cathodic polarization of pyrrhotite in soln. of potassium chloride. E. F. Smith observed that in the **electrolysis** of pyrrhotite in molten potassium hydroxide using an anode of platinum wire, and a nickel crucible as cathode, both the sulphur and iron are oxidized. R. Kremann and O. Bankovac studied the electrolysis of the molten sulphide.

An alternative name for pyrrhotite is magnetic pyrites, in allusion to its **magnetic properties**; but, according to E. Cohen,<sup>16</sup> and L. H. Borgström, troilite

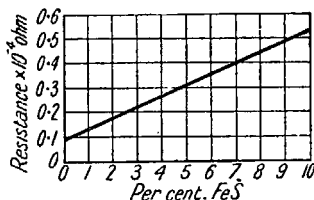


FIG. 612.—The Electrical Resistance of Solutions of Ferrous Sulphide in Iron.

or ferrous sulphide is non-magnetic, and when it appears to have magnetic properties, in meteorites, this is due to the presence of admixed nickeliferous iron. G. Wiedemann observed that precipitated ferrous sulphide has very feeble magnetic properties; and S. Veil found that the sulphide precipitated and washed in the cold is less magnetic than when it has been washed with hot water. M. Faraday observed that at the temp. of solid carbon dioxide, ferrous sulphide has no magnetization. R. J. Haüy, and C. C. Leonhard knew that pyrrhotite may exhibit polar magnetism, and the magnetic properties were observed by A. Frenzel, A. Delesse, C. B. Greiss, R. Juza and W. Biltz, F. Coeterier, A. Liversidge, O. Mügge, G. A. Kennigott, P. A. von Sachsen-Coburg, and T. Sidot; and C. Hatchett, and L. Bucca examined the effect of the sulphur content on the magnetic properties; and H. How noticed that the strength of the magnetization decreases with the proportion of contained nickel. F. Gieseler said that the synthetic sulphide is non-magnetic, but J. B. Peel and co-workers found the product to be magnetic when the ratio Fe : S is below that required for FeS.

E. T. Allen and co-workers showed that both allotropes of pyrrhotite exhibit polar magnetism, and that with  $\alpha$ -pyrrhotite, both poles lie along the  $a$ -axis; and with  $\beta$ -pyrrhotite, along the  $c$ -axis. A. Streng observed that the pyrrhotite of Bodenmais exhibits polar magnetism, with the north pole on the basal surfaces; if the north pole be stroked with the north pole of a magnet, it is reversed. This subject was discussed by P. Weiss and co-workers, A. Abt, R. H. de Waard, M. Ziegler, and W. Steinhaus and E. Gumlich. A. Streng, and G. Meslin observed that sections of pyrrhotite cut perpendicular to the principal axis are paramagnetic; and P. Weiss showed that the mineral is paramagnetic in the direction of the prismatic axis, and ferromagnetic in a plane perpendicular to that axis. P. Weiss and co-workers found that a crystal of pyrrhotite from Morro Velho, Brazil, exhibited zero magnetization when taken vertical to the base, ferromagnetism in the direction of the magnetic plane, and paramagnetism if vertical to that plane; it was inferred that the crystals of pyrrhotite consist of three simple crystals whose magnetic planes differ from the common plane by  $120^\circ$ . The molecular magnets were supposed to be arranged on a plane perpendicular to the trigonal axis. J. Beckenkamp added that if this were so, three or six such molecular magnets would correspond with a solid trigonal symmetry. The theory was discussed by P. Weiss and co-workers, and by K. Honda and J. Okubo. W. Sucksmith sought for a gyromagnetic effect with pyrrhotite, but the effective magnetization being only 5 per cent. that of magnetite, under similar conditions, the effect was not perceptible.

As a rule, the **magnetic susceptibility** of pyrrhotite is smaller than that of magnetite, but A. Abt found a crystal, approximating  $\text{Fe}_7\text{S}_8$ , which had a higher susceptibility than magnetite. The ratios of the sp. magnetism of hæmatite : pyrrhotite : magnetite are as 1 : 1.423 : 5.294. B. Bavink found the susceptibility of magnetite to be ten times greater than that of pyrrhotite. F. Stutzer and co-workers gave for the vol. susceptibility of pyrrhotite  $7018.0 \times 10^{-6}$ ; and P. Weiss gave  $175 \times 10^{-6}$  mass unit; and for the atomic susceptibility of the iron, 0.0098, a value close to that obtained for other paramagnetic compounds of iron. The susceptibility above  $300^\circ$  does not change with temp. N. R. Crane gave  $6.23 \times 10^{-6}$  mass unit. The subject was studied by A. Michel and G. Chaudron, D. R. Inglis, G. Grenet, J. Kunz, and W. Lenz. A. Streng, A. Abt, and G. Wiedemann measured the coercive force of pyrrhotite; and the remanences with a current of 48, 6.7, and less amperage, flowing through a copper spiral, about a parallelepiped of pyrrhotite, were respectively 0.08741, 0.00900, and 0.00671. A. Abt gave for the magnetic moment,  $M = 93.868$  c.g.s. units, and for a weight  $w = 77.73$  grms., the sp. magnetism  $M/w = 1.21$ . S. Wologdine found that pyrrhotite loses its ferromagnetism at about  $300^\circ$ . The subject was studied by F. Coeterier, and H. Ehrenberg. J. Huggett and G. Chaudron observed that when pyrrhotite is heated in air above  $250^\circ$  it exhibits first an increase and then an

irregular decrease in magnetization up to  $340^{\circ}$ . P. Weiss and co-workers located the **Curie point** at  $348^{\circ}$ , and later at  $318^{\circ}$  to  $319^{\circ}$ . M. Ziegler found that the magnetization curve rises from the temp. of liquid air, exhibits a maximum at  $-113^{\circ}$ , and then decreases parabolically to  $320^{\circ}$ , when it abruptly ceases. After cooling a crystal which had been heated above the Curie point, M. Ziegler observed a marked decrease in its magnetizability. The effect of temp. was also discussed by K. Honda and J. Okubo, and J. Forrest; the magnetic anisotropy, by F. Bloch and G. Gentile; the gyromagnetic effect, by W. Sucksmith—*vide* the magnetism of iron.

**The chemical properties of ferrous sulphide and of pyrrhotite.**—In nature, pyrrhotite alters into pyrite, marcasite, and arsenical pyrites. O. Müller<sup>17</sup> described pseudomorphs of copper pyrites; O. Mügge, arsenical pyrites; F. A. Genth, hisingerite; G. H. Smith, brown iron ore or pyrite; F. Schöndorf and R. Schroeder, J. E. Pogue, J. R. Blum, and A. Lacroix, marcasite; P. von Jereméeff, a mixture of marcasite and pyrite; E. Döll, magnetite; and O. Mügge, cuprite—all after pyrrhotite. Pyrrhotite also readily changes on weathering into limonite, goethite, hæmatite, and iron sulphates. This subject was discussed by F. Senft, J. Roth, G. W. Hawes, D. Forbes, H. Hilpert, G. Gilbert, A. A. Julien, etc.

H. Rose<sup>18</sup> observed that ferrous sulphide is not affected by heating it to redness in **hydrogen**; and F. von Schaffgotsch noticed that when ferrous sulphide is formed by heating magnetic pyrites in hydrogen, the product is non-magnetic. Apparently working at a higher temp., G. P. Schweder observed that the sulphide is reduced:  $\text{FeS} + \text{H}_2 \rightleftharpoons \text{Fe} + \text{H}_2\text{S}$ . K. Jellinek and J. Zakowsky calculated the thermal value of the reduction between  $730^{\circ}$  and  $910^{\circ}$  to be  $-10.24$  Cals., and between  $910^{\circ}$  and  $1100^{\circ}$ , to be  $-10.56$  Cals. E. V. Britzke and A. F. Kapustinsky found the equilibrium constant  $K$  in the system  $\text{FeS} + \text{H}_2 \rightleftharpoons \text{H}_2\text{S} + \text{Fe}$ , where  $K = p_{\text{H}_2\text{S}}/p_{\text{H}_2}$ , to be 0.0008 at  $723^{\circ}$ ; 0.0012 at  $800^{\circ}$ ; 0.00185 at  $897^{\circ}$ ; 0.0037 at  $994^{\circ}$ ; and also  $\log K_p = \log p_{-\text{H}_2\text{S}}/p_{-\text{H}_2} p_{\text{S}_2}^{1/2} = (19,200 - 0.94 \log T - 0.00165T + 0.037T^2 + 1.60)/4.571$ . S. Miyamoto found that the sulphide is reduced by hydrogen, in the silent discharge. F. Fischer and H. Tropsch observed that when iron sulphide is treated with hydrogen sulphide in the presence of steam, a small proportion of sulphur combines with the hydrogen without the steam exerting any oxidizing action, but in the absence of steam, no hydrogen sulphide is formed. J. J. Berzelius observed that moist ferrous sulphide readily oxidizes in **air** with the separation of sulphur, and the heat evolved may be great enough for incandescence; hence, added L. Gedel, the moist sulphide is best dried in an atm. of carbon dioxide. P. de Clermont and H. Guiot added that a rise of temp. up to  $50^{\circ}$  occurs when the moist sulphide is rubbed between the fingers; and E. Jordis and E. Schweizer observed that when triturated in a mortar, the mass becomes incandescent, and if the excess of sulphur be extracted from the precipitate, by benzene, or carbon disulphide, the residue may be pyrophoric. R. Scheuer found that the freshly-prepared sulphide, cooled out of contact with air, is fairly stable in air. The reaction was studied by H. Saito, and B. Neumann and W. Langer. A. Gélis, A. Wagner, H. le Chatelier and A. Ziegler, and E. Pollacci showed that a little sulphuric acid may be formed when the moist sulphide oxidizes in air; and that raising the temp. to  $100^{\circ}$  favours the production of sulphuric acid. E. T. Allen and J. Johnston observed the formation of some ferrous sulphate when pyrrhotite is triturated in a mortar. S. Veil found that ferrous sulphide, precipitated in the cold, and washed with cold water, is far more susceptible to oxidation than when it has been washed with hot water. W. Gluud and W. Reise found that ferrous sulphide is more slowly oxidized when suspended in water through which air is bubbled than is the case with ferrous oxide; and an increasing alkalinity in the sodium carbonate soln. in which the sulphide is suspended, retards the oxidation; the oxidation is favoured by raising the temp. from  $20^{\circ}$  to  $40^{\circ}$ . Ferrous sulphide precipitated from ferric oxide suspensions is more readily oxidized than that made



from ferrous oxide. This may be due to the presence of ferric sulphide. P. B. Ganguly and N. R. Dhar observed that colloidal soln., in air and sunlight, are oxidized to form colloidal sulphur which is coagulated by further exposure to light. J. J. Berzelius observed that when pyrrhotite is gently heated in air, some ferrous sulphate is formed, but at a higher temp., sulphur dioxide is given off and ferric oxide remains. F. Warlimont observed the formation of sulphate at 400°, and F. Schmitz, at 600° to 700°. J. S. C. Wells, H. Vestner, and F. Strohmeier added that if the roasting occurs at about 200°, ferrous oxide is produced, and at a red-heat, ferric oxide. K. Friedrich said that purified ferrous sulphide has a higher decomposition temp. than is the case when more sulphur is present as in the case of pyrrhotite and pyrites. The temp. of decomposition in a current of oxygen is 555°, and in a current of air, 535°, when the grain-size is 0.1 to 0.2 mm. diameter. The ferrous sulphide does not sinter or decrepitate, but pyrrhotite may decrepitate. Pyrrhotite (58.42, Fe; 37.10, S), of grain-size 0.1 to 0.2 mm., develops sulphur dioxide in oxygen at 533°, and in air at 525°; and H. Saito found that pyrrhotite approximating  $\text{Fe}_{10}\text{S}_{11}$ , and of grain-size 0.074 mm., begins to develop sulphur dioxide at 430°, and at 800°, the transformation to ferric oxide is complete. E. V. Britzke and A. F. Kapustinsky gave for the heat of oxidation or roasting,  $2\text{FeS} + 3\frac{1}{2}\text{O}_2 = \text{Fe}_2\text{O}_3 + 2\text{SO}_2 + 294.84$  Cals. V. Rodt observed that when hydrated ferrous sulphide is oxidized by exposure to air, yellow  $\text{FeO}(\text{OH})$  and free sulphur are formed, but no  $\text{FeS}_2$ . The oxidation was studied by R. C. Wells, B. Neumann and co-workers, C. R. van Hise, V. H. Gottschalk and H. A. Buehler, W. H. Emmons, F. Foreman, and S. H. Emmens—*vide infra*, pyrites.

F. Cornu found that moist pyrrhotite has a feeble acidic reaction. F. Carmichael found that 0.18 to 0.38 per cent. of sulphur and metal is oxidized when powdered pyrrhotite is agitated with water and oxygen for 13 days; similarly, 0.37 per cent. of troilite was oxidized. O. Weigel calculated the solubility of ferrous sulphide in water, from conductivity measurements at 18°, and obtained  $70.1 \times 10^{-6}$  mol per litre, and for pyrrhotite,  $53.6 \times 10^{-6}$  mol per litre; I. M. Kolthoff doubted the accuracy of these data. R. C. Wells obtained a smaller value, namely  $1.9 \times 10^{-11}$  mol per litre. The assumption is made that the sulphide which dissolves is completely hydrolyzed. A. Jouniaux gave  $5.35 \times 10^{-8}$  gram per litre for the solubility; L. Bruner and J. Zawadsky,  $10^{-5.9}$ ; and L. Moser and M. Behr,  $10^{-6.52}$ ; and they also gave for the solubility product  $3.7 \times 10^{-19}$  on the assumption that the equilibrium constant:  $[\text{Fe}^{++}][\text{H}_2\text{S}] = k[\text{H}^+]^2$ , is  $K = 3.4 \times 10^3$ . For the solubility in 0.01N- $\text{H}_2\text{SO}_4$ , L. Moser and M. Behr gave 0.0024 mol. per litre. I. M. Kolthoff discussed these results. F. Foreman reported that the solubility, S, parts per million, of pyrrhotite, when heated in sealed tubes, is as follows:

SOLVENT	Dissolved	100°	150°	250°	320°
Water . . . . .	{ Fe . . . . . Fe eq. of $\text{H}_2\text{S}$ . . . . .	0.00 —	0.02 13.1	0.00 32.4	0.33 62.4
0.1N- $\text{NaHCO}_3$ . . . . .	{ Fe . . . . . Fe eq. of $\text{H}_2\text{S}$ . . . . .	0.00 —	0.08 27.4	0.03 20.1	0.18 15.1
0.1N- $\text{Na}_2\text{S}$ . . . . .	{ Fe . . . . . Fe eq. of $\text{H}_2\text{S}$ . . . . .	0.00 —	0.00 20.1	0.00 30.2	0.00 32.4

H. V. Regnault, O. Schumann, and P. de Clermont and H. Guiot observed that when ferrous sulphide is boiled with water, some sulphuric acid and hydrogen are formed; and in an exhausted sealed tube at 56°, P. de Clermont and J. Frommel observed that some hydrogen sulphide is produced; and L. Benedek reported that some ferrous oxide is formed as well as ferric oxide. F. Hoppe-Seyler found that if a slurry is shaken in the presence of air and ammonia, some thiosulphate and sulphur are formed as well as hydrated iron oxide, but no nitrite is produced. H. V. Regnault found that when water vapour is passed over red-hot ferrous sul-

phide, hydrogen and hydrogen sulphide are given off, and a black, magnetic mass remains. The steam first forms hydrogen sulphide and ferrous oxide, and the ferrous oxide reacts with steam to form hydrogen and ferrosic oxide. Not all the sulphur is expelled after 3 hrs'. heating in steam. A. Gautier observed that with powdered ferrous sulphide, at approximately  $800^{\circ}$ , the gas contained 22 to 32 per cent.  $\text{H}_2\text{S}$  by vol., and 76 to 65 per cent.  $\text{H}_2$ ; but with a coarser-grained sulphide, the gas contained 98.94 per cent.  $\text{H}_2$  by vol., and 1.06 per cent.  $\text{H}_2\text{S}$ . The residue was ferrosic oxide. F. Fischer and H. Tropsch observed that at  $450^{\circ}$  to  $470^{\circ}$  the gas contained 97.3 per cent. of hydrogen by vol., and 2.1 per cent. of  $\text{H}_2\text{S}$ . A. Gautier found that above  $800^{\circ}$ , some hydrogen sulphide is oxidized to sulphuric acid. F. C. Thompson and N. Tilling studied the reaction:  $3\text{FeS} + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 3\text{H}_2\text{S} + \text{H}_2$ . E. Arbeiter, and J. F. Hernandez examined the action of **hydrogen dioxide** on precipitated ferrous sulphide, and found that in acidic soln., ferric sulphate, or the products of the hydrolysis of ferric sulphate are formed.

H. Moissan observed that **fluorine** in the cold does not act on ferrous sulphide, but at a dull red-heat, white ferric fluoride is formed, and the mass becomes white-hot. H. Rose showed that **chlorine** does not decompose ferrous sulphide in the cold, but E. Zielinsky said that the action starts below room temp., and when heated, sulphur monochloride and ferrous chloride are readily formed. According to L. E. Rivot and co-workers, chlorine oxidizes ferrous sulphide in alkaline soln., to form an alkaline ferrate (*q.v.*). J. Lemberg observed that in alkaline soln., **bromine** oxidizes pyrrhotite rapidly to hydrated ferric oxide. E. Filhol and J. Melliès found that **iodine** in contact with precipitated ferrous sulphide at ordinary temp. forms ferrous iodide and sulphur; the reaction is very slow when iodine acts on ferrous sulphide suspended in cold water, but very rapid if the water is boiling. The reaction with the native sulphide is slow at ordinary temp., but in a sealed tube at  $200^{\circ}$ , it is very rapid. H. Wurtz observed that unlike pyrite, pyrrhotite is slowly attacked by a freshly-prepared soln. of iodine, and the liquid is slowly decolorized. E. Zalinsky found that pyrrhotite is dissolved very slowly by **hydrofluoric acid**. G. Gore found that liquid **hydrogen chloride** does not attack ferrous sulphide. J. J. Ebelmen observed that ferrous sulphide, prepared at a red-heat by the action of hydrogen sulphide on ferric oxide, is scarcely affected by cold **hydrochloric acid**. As a rule, the mineral acids dissolve purified ferrous sulphide without residue, and with the evolution of hydrogen sulphide; in the case of hydrochloric acid, the dissolution of pyrrhotite may be attended by the separation of sulphur, and the soln. may have a yellow colour owing to the presence of traces of ferric hydroxide; and a green soln. may indicate the presence of nickel. The reaction was studied by A. Streng, and E. Arbeiter.

R. Scheuer observed that when ferrous sulphide is heated with **sulphur**, iron disulphide is formed between  $175^{\circ}$  and  $225^{\circ}$ ; ferric sulphide between  $400^{\circ}$  and  $450^{\circ}$ ; and pyrrhotite, above  $600^{\circ}$ . The reaction has been previously discussed in connection with the action of heat on ferrous sulphide, *vide* Fig. 608; and similarly also with **hydrogen sulphide**. G. N. Quam found that liquid hydrogen sulphide has no action on ferrous sulphide. L. L. de Koninck found that ferrous sulphide is insoluble in an aq. soln. of hydrogen sulphide, or **ammonium sulphide**, although it is slightly soluble in aq. soln. of **sodium or potassium sulphide**. A. Terrell found that pyrrhotite readily dissolves in a boiling soln. of sodium sulphide. H. Fincke studied the action of ferrous sulphide on fused sodium sulphide—*vide infra*. L. L. de Koninck and M. Ledent found that sodium polysulphide acts on ferrous sulphide forming a green soln. which W. Mecklenburg and V. Rodt said is stable at  $0^{\circ}$ ; at  $8^{\circ}$ , it precipitates ferrous sulphide completely. G. W. A. Foster said that with freshly-precipitated ferrous sulphide, a red soln. is formed which later becomes brown. A. Kanschegg and H. Malfatti observed that ferrous sulphide with ammonium sulphide in the presence of ammonium acetate produces a pale green soln.; and that precipitated ferrous sulphide dissolves in ammonium sulphide. H. Rose observed, contrary to the statement of J. F. Persoz, that ferrous sulphide

can be nearly completely precipitated by ammonium sulphide in the presence of sodium pyrophosphate. The Rhenania Verein Chemischer Fabriken showed that dry **sulphur dioxide** begins to act on ferrous sulphide at  $600^{\circ}$ , and the yield of sulphur in the reaction:  $3\text{FeS} + 2\text{SO}_2 = \text{Fe}_3\text{O}_4 + 5\text{S}$ , is about 70 per cent.; and at  $800^{\circ}$  to  $900^{\circ}$ , L. Wöhler and co-workers obtained a 100 per cent. yield. The thermal value of the reaction is small, for it amounts to about  $-17$  Cals. The reaction is accelerated in the presence of magnesia, or of ferrous oxide. V. M. Goldschmidt said that the reaction between sulphur dioxide and ferrous sulphide begins at  $580^{\circ}$ . According to J. Milbauer and J. Tucek, the reaction also progresses:  $\text{FeS} + 2\text{SO}_2 = \text{FeSO}_4 + \text{S}$ , and  $4\text{FeSO}_4 + \text{S} = 2\text{Fe}_2\text{O}_3 + 5\text{SO}_2$ , and the relative proportions of ferrous sulphate and ferric oxide at different temp., are:

	500°	600°	700°	800°
$\text{FeSO}_4$	22.75	19.84	13.46	—
$\text{Fe}_2\text{O}_3$	8.97	39.35	80.79	99.63

E. Diepschlag and E. Horn represented the reaction which occurs at  $800^{\circ}$  by  $3\text{FeS} + 2\text{SO}_2 = \text{Fe}_3\text{O}_4 + 5\text{S}$ . A. C. Halferdahl calculated for the free energy of the reaction:  $3\text{FeS} + 2\text{SO}_2 = \text{Fe}_3\text{O}_4 + 2\frac{1}{2}\text{S}_2$ , 6800 cal. at  $600^{\circ}$ , and 5800 cal. at  $1400^{\circ}$ ; and for  $2\text{FeS} + \text{SO}_2 = 2\text{FeO} + 1\frac{1}{2}\text{S}_2$ , 14,500 cal. at  $600^{\circ}$ , and 2400 cal. at  $1400^{\circ}$ . According to A. Guerout, when sulphur dioxide acts on ferrous sulphide suspended in water, some heat is developed, and hydrogen sulphide, sulphur, and thiosulphate are formed. W. E. Henderson and H. B. Weiser represented the reaction  $\text{FeS} + \text{H}_2\text{SO}_3 = \text{H}_2\text{S} + \text{FeSO}_3$ , and some thiosulphate is also produced. If the slurry of ferrous sulphide be added to conc. **sulphurous acid**, the excess of sulphur dioxide oxidizes the hydrogen sulphide, and prevents the formation of ferrous sulphite; so that the reaction is represented:  $2\text{FeS} + 3\text{SO}_2 = 2\text{FeS}_2\text{O}_3 + \text{S}$ . F. Förster and J. Janitzky studied the reaction. W. Feld observed the formation of tetrathionate in neutral soln.:  $\text{FeS} + 3\text{SO}_2 = \text{FeS}_4\text{O}_6$ , and F. Förster and J. Janitzky observed the formation of the following relative proportions:  $\text{S}_2\text{O}_3''$ , 5.2 millimols;  $\text{S}_3\text{O}_6''$ , 0.1;  $\text{S}_4\text{O}_6''$ , 1.8;  $\text{S}_5\text{O}_6''$ , 0.8; and S, 3.0. L. L. de Koninck noted the solubility of ferrous sulphide in sulphurous acid. H. B. North and C. B. Conover represented the action of **thionyl chloride** in a sealed tube at  $150^{\circ}$  to  $200^{\circ}$ , by the equation:  $6\text{FeS} + 16\text{SOCl}_2 = 6\text{FeCl}_3 + 8\text{SO}_2 + 7\text{S}_2\text{Cl}_2$ . H. Danneel and F. Schlottmann studied the action of **sulphuryl chloride**. L. Moser and M. Behr observed that a litre of 0.1*N*-**sulphuric acid**, sat. with hydrogen sulphide, dissolved 0.2136 gm. FeS, or  $2.4 \times 10^{-3}$  mol, at  $20^{\circ}$ . The effect of hydrogen sulphide in the soln. under press. has been previously discussed, G. Bruni and M. Padoa suggested that possibly some polysulphide is formed. According to G. S. Nishihara, the attackability of pyrrhotite by 0.125*N*- $\text{H}_2\text{SO}_4$  is 100, when that of pyrite is unity; and R. C. Wells obtained a similar result. P. Casamajor found that the dissolution of ferrous sulphide in dil. sulphuric acid is favoured by the presence of zinc. According to A. Lipschitz and R. von Hasslinger, purified ferrous sulphide reacts only extremely slowly with cold, dil. acids. "Active" ferrous sulphide, which evolves hydrogen sulphide with cold dil. acids, contains metallic iron; the hydrogen formed by the action of the acid on the free iron reduces the ferrous sulphide to hydrogen sulphide and iron, so that a small amount of free iron acts as an accelerator of the reaction. A. E. H. Tutton found that **selenic acid** converts ferrous sulphide into ferrous selenate and hydrogen sulphide is evolved; V. Lenher and C. H. Kao, that **selenium monochloride** at  $100^{\circ}$ , forms ferrous chloride with the liberation of sulphur and selenium; and V. Lenher, that **selenyl bromide** forms ferric bromide and selenium monobromide.

E. C. Franklin and C. A. Kraus found ferrous sulphide to be insoluble in liquid **ammonia**. Ferrous sulphide is insoluble in aq. ammonia. P. de Clermont observed that precipitated ferrous sulphide is easily dissolved by soln. of **ammonium salts**; although R. H. Brett said that the ordinary sulphide is insoluble in soln. of ammonium nitrate or chloride; R. Lorenz found that when ferrous sulphide is

heated with ammonium chloride, some ferrous chloride is volatilized. P. de Clermont found that ammonium salts of organic acids—oxalic, tartaric, and succinic—form the corresponding ferrous salts when they act on ferrous sulphide. T. W. B. Welsh and H. J. Broderson showed that 100 grms. of **hydrazine** dissolve 9 grms. of ferrous sulphide with decomposition at room temp. J. J. Berzelius found that **nitric acid** dissolves ferrous sulphide forming nitric oxide; and C. Hatchett, that nitric acid of sp. gr. 1.38 diluted with an equal vol. of water, does not act on pyrrhotite in the cold, but when the acid is heated, the sulphide dissolves. S. Meunier observed that troilite is not attacked by cold, fuming nitric acid. R. F. Weinland and L. Storz found that **sodium arsenite** acts on ferrous sulphide, and pyrrhotite forming ferric oxide and hydrogen sulphide which reacts with the arsenite to form sulphoarsenite; L. Storch found that ferrous sulphide is soluble in soln. of **alkali sulphoarsenates, sulphoantimonates, sulphovanadates, sulphostannates, sulphomolybdates, and sulphotungstates.**

Ferrous sulphide is reduced to the metal when it is heated with **carbon**; and, according to N. Parravano and G. Malquori, the formation of carbon disulphide:  $2\text{FeS} + \text{C} = \text{CS}_2 + 2\text{Fe}$ , begins at about  $1200^\circ$ . O. Meyer noted that **silicon carbide** is attacked by ferrous sulphide at  $1200^\circ$ . T. Sato, and H. Hanemann and A. Schildkötter studied the action of **iron tritacarbide** in the quasiternary system Fe-FeS- $\text{Fe}_3\text{C}$ , and found a ternary eutectic at  $975^\circ$  with 10.5 per cent. Fe, 87 per cent. FeS, and 2.5 per cent.  $\text{Fe}_3\text{C}$ . No ternary solid soln. was observed at the  $\text{Fe}_3\text{C}$  corner of the ternary diagram; and only a small range in the iron corner as the solid solubility of sulphur in iron does not exceed about 0.03 per cent. The solubility of iron in ferrous sulphide at the ternary eutectic temp. is about 3 per cent., and that of  $\text{Fe}_3\text{C}$  in iron at the same temp. is 20 per cent. Molten mixtures having a composition indicated by any point on the straight line joining the Fe- $\text{Fe}_3\text{C}$  eutectic to the Fe-FeS eutectic in the triangular diagram, separate into two liquid phases—the upper one containing 0.22 per cent. C and 30.65 per cent. S, and the lower one, 4.12 per cent. C and 0.98 per cent. S. In Fig. 613, O represents the ternary system with 87 per cent. FeS, 2.5 per cent.  $\text{Fe}_3\text{C}$ , and 10.5 per cent. Fe;  $E_1$ ,  $E_2$ , and  $E_3$  represent binary eutectics; DF, the line of separation of the heterogeneous two-phase solid soln. of iron and iron sulphide from the heterogeneous three-phase soln. F represents the conc. of the sat. soln. with 97 per cent. of FeS. K. Stammer said that **carbon monoxide** does not act on ferrous sulphide; and A. Foss and B. J. Halvorsen observed that **carbon dioxide** reacts furnishing ferric oxide, carbon monoxide and sulphur dioxide; the reaction begins at  $600^\circ$ , and progresses best at about  $1000^\circ$  when the reacting mass does not fuse. M. Costeanu said that at  $1000^\circ$ , the reaction progresses:  $\text{FeS} + \text{CO} = \text{FeO} + \text{CO} + \text{S}$ , and at  $1100^\circ$ ,  $3\text{FeS} + 4\text{CO}_2 = \text{Fe}_3\text{O}_4 + 4\text{CO} + 3\text{S}$ . V. M. Goldschmidt found that the reaction:  $\text{FeS} + 3\text{CO}_2 = \text{FeO} + 3\text{CO} + \text{SO}_2$  does not occur below  $630^\circ$ , and a temp. of  $1150^\circ$  is necessary for an appreciable reaction. F. von Schaffgotsch observed that no sulphur is dissolved when pyrrhotite is shaken with **carbon disulphide**, although C. Bodewig, and E. Jordis and E. Schweizer said that some sulphur is dissolved. T. Sato studied the system with iron and **iron carbide**. J. Lemberg observed that ferrous sulphide is soluble in a soln. of **potassium cyanide**; and with a boiling soln., L. T. Wright, G. W. A. Foster, and T. G. Pearson and P. L. Robinson observed that some potassium ferrocyanide is formed. W. Wanjukoff observed that only traces of the sulphide are dissolved by a sat. soln. of potassium cyanide, and N. Juschkevitch found the sulphide to be insoluble in a 7 per cent.

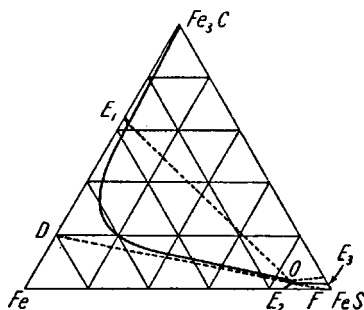


FIG. 613.—The Ternary System: Fe-FeS- $\text{Fe}_3\text{C}$ .

Fe, 87 per cent. FeS, and 2.5 per cent.  $\text{Fe}_3\text{C}$ . No ternary solid soln. was observed at the  $\text{Fe}_3\text{C}$  corner of the ternary diagram; and only a small range in the iron corner as the solid solubility of sulphur in iron does not exceed about 0.03 per cent. The solubility of iron in ferrous sulphide at the ternary eutectic temp. is about 3 per cent., and that of  $\text{Fe}_3\text{C}$  in iron at the same temp. is 20 per cent. Molten mixtures having a composition indicated by any point on the straight line joining the Fe- $\text{Fe}_3\text{C}$  eutectic to the Fe-FeS eutectic in the triangular diagram, separate into two liquid phases—the upper one containing 0.22 per cent. C and 30.65 per cent. S, and the lower one, 4.12 per cent. C and 0.98 per cent. S. In Fig. 613, O represents the ternary system with 87 per cent. FeS, 2.5 per cent.  $\text{Fe}_3\text{C}$ , and 10.5 per cent. Fe;  $E_1$ ,  $E_2$ , and  $E_3$  represent binary eutectics; DF, the line of separation of the heterogeneous two-phase solid soln. of iron and iron sulphide from the heterogeneous three-phase soln. F represents the conc. of the sat. soln. with 97 per cent. of FeS. K. Stammer said that **carbon monoxide** does not act on ferrous sulphide; and A. Foss and B. J. Halvorsen observed that **carbon dioxide** reacts furnishing ferric oxide, carbon monoxide and sulphur dioxide; the reaction begins at  $600^\circ$ , and progresses best at about  $1000^\circ$  when the reacting mass does not fuse. M. Costeanu said that at  $1000^\circ$ , the reaction progresses:  $\text{FeS} + \text{CO} = \text{FeO} + \text{CO} + \text{S}$ , and at  $1100^\circ$ ,  $3\text{FeS} + 4\text{CO}_2 = \text{Fe}_3\text{O}_4 + 4\text{CO} + 3\text{S}$ . V. M. Goldschmidt found that the reaction:  $\text{FeS} + 3\text{CO}_2 = \text{FeO} + 3\text{CO} + \text{SO}_2$  does not occur below  $630^\circ$ , and a temp. of  $1150^\circ$  is necessary for an appreciable reaction. F. von Schaffgotsch observed that no sulphur is dissolved when pyrrhotite is shaken with **carbon disulphide**, although C. Bodewig, and E. Jordis and E. Schweizer said that some sulphur is dissolved. T. Sato studied the system with iron and **iron carbide**. J. Lemberg observed that ferrous sulphide is soluble in a soln. of **potassium cyanide**; and with a boiling soln., L. T. Wright, G. W. A. Foster, and T. G. Pearson and P. L. Robinson observed that some potassium ferrocyanide is formed. W. Wanjukoff observed that only traces of the sulphide are dissolved by a sat. soln. of potassium cyanide, and N. Juschkevitch found the sulphide to be insoluble in a 7 per cent.

soln. G. P. Lewis represented the reaction in the presence of potassium carbonate:  $2K_2CO_3 + FeS + 6HCy = K_4FeCy_6 + H_2S + 2CO_2 + 2H_2O$ . H. L. Dunlap found that when heated 2 hrs., at  $340^\circ$ , with **paraffin**, a little hydrogen sulphide is evolved, and the residue is magnetic. E. Jordis and E. Schweizer observed that **benzene**, and **alcohol** extract some sulphur from ferrous sulphide when treated for several days in an extraction apparatus. M. Berthelot found that **ether** extracts sulphur from ferrous sulphide, and pyrrhotite. A. Naumann observed that ferrous sulphide is insoluble in **methyl acetate**; and A. Naumann, and M. Hamers, in **ethyl acetate**. F. Stolle showed that 10, 30, and 50 per cent. soln. of **sugar** dissolve respectively 3.8, 7.1, and 9.9 mgrms. of ferrous sulphide per litre at  $17.5^\circ$ ; 3.8, 9.1 and 19.8 mgrms. respectively at  $45^\circ$ ; and 5.3, 7.2, and 9.1 mgrms. respectively at  $75^\circ$ . A. Naumann and J. Schröder found that ferrous sulphide is insoluble in **pyridine**. G. Röhl observed that an alcoholic soln. of **picric acid** colours deep blue on a yellow ground, inclusions of ferrous sulphide in steel which has been quenched from a yellow heat. H. C. Bolton found that pyrrhotite is attacked in the cold by **citric acid**, and some hydrogen sulphide is evolved. J. Spiller said that ferrous sulphide is not completely precipitated in the presence of **sodium citrate**. T. Turner, and K. Hilgenstock observed no reaction between **silicon** or **ferrosilicon** and fused ferrous sulphide. W. P. Jorissen and B. L. Ongkiehong, and J. H. Andrew and W. R. Maddocks examined the effect of **silica** on the reaction between sulphur and iron. W. Jander, and W. Jander and K. Rothschild studied the action of various **metal silicates**—lead, copper, and nickel—on ferrous sulphide; and W. Jander and co-workers, and B. P. Selwanoff and co-workers, of **ferrous silicate**. W. Treitschke and G. Tammann said that **porcelain** is attacked strongly when heated with ferrous sulphide, but K. Friedrich observed that the sulphide alone does not attack porcelain, it does so only when partially oxidized. E. T. Allen and co-workers observed no attack when air is excluded. A. Cayphas studied the action of furnace slags on iron sulphide.

A. Colson observed that a polished piece of ferrous sulphide resting on a **copper** plate, in an atm. of carbon dioxide, gives up some sulphur to the copper. K. Hilgenstock, and A. Ledebur discussed alloys of ferrous sulphide and copper. The reaction was studied by A. Baykoff. B. Garre found that when ferrous sulphide is heated with **magnesium**, a reaction:  $FeS + Mg = MgS + Fe$ , begins at  $470^\circ$ , which is violent at  $670^\circ$ , and the thermal value is 56.3 Cals. H. Ditz observed that with **aluminium** in the thermite process:  $3FeS + 2Al = Al_2S_3 + 3Fe$ , about 25 per cent. remains in the slag as  $FeS \cdot Al_2S_3$ . The reaction was also discussed by G. Tammann and H. Bohner, T. R. Haglund, K. Hilgenstock, F. A. Livermore, A. Ledebur, A. McCance, and N. Parravano and P. Agostini. K. Hilgenstock, and A. Ledebur found that **chromium** acts on molten ferrous sulphide removing some of the sulphur, and forming a slag. H. von Jüptner observed that ferrous sulphide is decomposed when it is heated with **manganese** since the press. of the sulphur is smaller with manganese sulphide than it is with ferrous sulphide. The reaction  $FeS + Mn = Fe + MnS$  is exothermal, and it is utilized in the desulphurization of steel—*vide supra*, action of sulphur on **iron**. The reversible reaction was studied by K. Hilgenstock, A. Ledebur, R. Vogel and H. Baur, G. Tammann and H. Bohner, and C. H. Herty and O. S. True. G. P. Schweder observed that molten ferrous sulphide can dissolve some iron; and the solubility of ferrous sulphide in steel was discussed by J. H. Andrew and D. Binnie. P. Berthier observed that when the molten mixture of ferrous sulphide and iron is cooled, two layers are formed, and they are easily separated by a blow from a hammer—*vide supra*, Fig. 604. K. Hilgenstock, A. Ledebur, and J. H. L. Vogt observed that **nickel** acts on molten ferrous sulphide:  $FeS + Ni \rightleftharpoons NiS + Fe$ ; and J. H. L. Vogt said that the reaction is similar with **cobalt**.

A. Kanschegg and H. Malfatti found that ferrous sulphide is insoluble in an aq. soln. of **alkali hydroxide**, but if sulphur be present, added purposely, or brought in when the ferrous sulphide has been formed by adding ammonium polysulphide

to a soln. of ferric chloride, a dark green soln. is formed, which, as suggested by L. L. de Koninck, as in many other cases is probably a case of the peptization of the colloid. A. Konschegg and H. Malfatti supposed, however, that the dissolution is due to the formation of a thioferrate. J. D. Clark and P. L. Menaul found that with pyrrhotite ground to pass a lawn of 0.05 mm. mesh, 0.01*N*-KOH begins to form a colloidal soln. in about 6 days, and in 67 days, 2.22 per cent. of the mineral is in colloidal soln. They also discussed the effect of lime and alumina on the reaction. A. Terreil, and C. F. Becker observed that a brown soln. is frequently produced at first, and this turns green on exposure to air. The reaction was shown by L. L. de Koninck, and A. Villiers to be so very sensitive that if the  $\text{FeS} : \text{KOH} = 1 : 4,000,000$  the coloration appears. P. Berthier found that when ferrous sulphide is heated to low redness with about twice its weight of **alkali carbonate**, a black, crystalline, magnetic mass is formed from which water extracts alkali sulphide containing a trace of sulphate; if the mixture is heated to whiteness in a carbon crucible, cast iron is formed. R. Finkener showed that the desulphurization of ferrous sulphide by **calcium oxide** is an important reaction in the blast-furnace; calcium oxide alone does not act on ferrous sulphide; but it does so in the presence of reducing agents—*e.g.*, G. Hilgenstock, and B. Osann found that with hydrogen, the reaction is symbolized:  $\text{FeS} + \text{CaO} + \text{H}_2 = \text{CaS} + \text{Fe} + \text{H}_2\text{O}$ ; A. Ledebur, with carbon:  $\text{FeS} + \text{CaO} + \text{C} = \text{CaS} + \text{Fe} + \text{CO}$ ; and B. Osann, with carbon monoxide:  $\text{FeS} + \text{CaO} + \text{CO} = \text{CaS} + \text{Fe} + \text{CO}_2$ . G. Tammann and H. O. von Samson-Himmelstjerna observed that the heat of the reaction:  $\text{FeS} + \text{RO} = \text{FeO} + \text{RS}$ , is 1.9 Cals. with calcium oxide, 11.1 Cals. with **strontium oxide**, 15.6 Cals. with **barium oxide**, and -1.5 Cals. with **zinc oxide**. H. N. Stokes found that precipitated ferrous sulphide does not react with an ammoniacal soln. of **zinc hydroxide** in the cold, or at the b.p., but between 160° and 170°, there is a slow reaction forming colourless ferrous hydroxide and zinc sulphide. T. R. Haglund represented the reaction with **alumina**:  $\text{Al}_2\text{O}_3 + 3\text{FeS} + 3\text{C} = \text{Al}_2\text{S}_3 + 3\text{Fe} + 3\text{CO}$ . P. Berthier observed that when ferrous sulphide is fused with 30 times its weight of **lead oxide**, sulphur dioxide is evolved, and lead, and a slag containing lead and ferrous oxide are produced; and with 5 times its weight of lead oxide, the mixture swells up when strongly heated to form a grey, homogeneous, magnetic slag containing sulphides of iron and lead. G. Tammann and H. O. von Samson-Himmelstjerna found for the heat of the reaction:  $\text{FeS} + \text{PbO} = \text{PbS} + \text{FeO} + 10.6$  Cals., and with **manganese oxide**, -2.8 Cals. B. Osann, and H. Skappel showed that manganese oxide and carbon react on ferrous sulphide:  $\text{FeS} + \text{MnO} + \text{C} = \text{Fe} + \text{MnS} + \text{CO}$ . J. H. L. Vogt said that **ferrosic oxide** is nearly insoluble in molten ferrous sulphide. F. S. Wartman and G. L. Oldright observed a small reduction of magnetite by ferrous sulphide at 1000°, and the reduction was rapid at higher temp. Orthoclase, albite, anorthite, china-clay, silica, and magnesia accelerate the reaction, whereas the reaction is retarded by lime, alumina, and cuprous sulphide. A. C. Halferdahl calculated for the reaction  $4\text{Fe}_3\text{O}_4 + \text{FeS} = 13\text{FeO} + \text{SO}_3$ , the free energy 97,300 cals. at 600°, and 35,100 cals. at 1400°; for  $3\text{Fe}_3\text{O}_4 + \text{FeS} = 10\text{FeO} + \text{SO}_2$ , 52,200 cals. at 600°, and -5300 cals. at 1400°; and for  $\text{Fe}_3\text{O}_4 + \text{FeS} = 4\text{FeO} + \frac{1}{2}\text{S}_2$ , 22,200 cals. at 600°, and -900 cals. at 1400°. G. Tammann and H. O. von Samson-Himmelstjerna gave:  $3\text{FeS} + 2\text{Fe}_2\text{O}_3 = 7\text{Fe} + 3\text{SO}_2 - 48.6$  Cals.; and for  $\text{FeS} + 2\text{FeO} = 3\text{Fe} + \text{SO}_2 - 83.0$  Cals. E. D. Campbell obtained what might have been impure **ferric oxysulphide**,  $\text{Fe}_2\text{OS}_2$ , by melting together a mixture of ferrosic oxide and ferrous sulphide. C. F. Rammelsberg obtained what he regarded as an oxysulphide by the action of hydrogen sulphide on ferric oxide below redness, and F. Martin and O. Fuchs, and L. Wöhler and co-workers represented the reaction at 900° to 1000° by the equation:  $\text{FeS} + 3\text{Fe}_3\text{O}_4 = 10\text{FeO} + \text{SO}_2$ ; and the reaction with **ferric oxide**, which begins at 550° and is completed at 800°, by  $\text{FeS} + 10\text{Fe}_2\text{O}_3 = 7\text{Fe}_3\text{O}_4 + \text{SO}_2$ —the ferrosic oxide at a higher temp. reacts as indicated above. P. Tschirwinsky, A. C. Halferdahl, and E. Diepschlag and E. Horn studied the reaction. The reaction with ferric oxide commences at 550° and is complete at 800° to 850°.

Between 850° and 1100° no reaction occurs between ferrosic oxide and ferrous sulphide, but at higher temp. the reaction:  $\text{FeS} + 3\text{Fe}_3\text{O}_4 = 10\text{FeO} + \text{SO}_2$  takes place, 77.5 per cent. of the iron being converted into ferrous oxide at 1220°; above 1300°, a small amount of free sulphur is formed and the solid product contains traces of metallic iron. L. T. Wright represented the heat of the reaction with ferric oxide by 86.2 Cals. A. C. Halferdahl calculated for the reaction:  $4\text{Fe}_2\text{O}_3 + \text{FeS} = 9\text{FeO} + \text{SO}_3$  the free energy 52,100 cals. at 600°, or 9500 cals. at 1400°; for  $4\text{Fe}_2\text{O}_3 + \text{FeS} = 3\text{Fe}_3\text{O}_4 + \frac{1}{2}\text{S}_2$ , -8300 cals. at 600°, and -29,700 cals. at 1400°; and for  $10\text{Fe}_2\text{O}_3 + \text{FeS} = 7\text{Fe}_3\text{O}_4 + \text{SO}_2$ , -24,200 cals. at 600°, and -82,300 cals. at 1400°. P. Tschirwinsky said that the eutectic with ferrous sulphide and **ferrous oxide** (4:1) is at 1060°. A. C. Halferdahl calculated for the reaction:  $2\text{FeO} + \text{FeS} = \text{SO}_2 + 3\text{Fe}$ , the free energy 53,000 cals. at 600°, and 23,500 cals. at 1400°, but the reaction does not proceed spontaneously. H. le Chatelier and A. Ziegler also studied the subject. G. P. Schweder fused a mixture of **nickel oxide** and ferrous sulphide under borax, and obtained a magnetic, brass-yellow mass containing nickel oxide and sulphide.

G. Buchner found that a boiling soln. of **sodium pyrosulphate** dissolves ferrous sulphide to form a colourless soln., which, when cold, is green. A. Gorgeu found that molten **sodium sulphate** oxidizes ferrous sulphide to ferrosic oxide; and M. Websky found that molten **potassium hydrosulphate** dissolves ferrous sulphide forming a deep brown mass which is pale yellow when cold. F. Raschig, and C. Meinecke observed that a soln. of **cuprous chloride** in the presence of sodium chloride gives with ferrous sulphide a precipitate of cuprous sulphide; and a soln. of **cupric chloride** furnishes ferrous chloride and cupric sulphide. W. F. K. Stock said that a boiling, ammoniacal soln. of cuprous chloride transforms 80 per cent. of ferrous sulphide to chloride. E. F. Anthon, and L. T. Wright also observed that hydrated ferrous sulphide precipitates copper sulphide from soln. of copper salts. E. F. Anthon, L. T. Wright, P. L. Robinson and co-workers, and O. Ruff and B. Hirsch observed that cold, and boiling soln. of **copper sulphate** give a precipitate of copper sulphide; but S. Meunier added that troilite is not attacked. The active and inactive forms of ferrous sulphide observed by A. Lipschitz and R. von Hasslinger, were discussed above. F. F. Grout observed that some varieties of pyrrhotite act slowly on an acidic soln. of copper sulphate, and some varieties do not act at all—and this, added G. S. Nishihara, even at a high temp. E. G. Zies and co-workers reported that natural or artificial pyrrhotite, when heated 3 days with a 5 per cent. soln. of copper sulphate, at 200°, is converted into copper pyrites,  $\text{CuFeS}_2$ . C. Palmer and E. S. Bastin found that pyrrhotite reduces soln. of **silver salts**; J. Lemberg observed that a sulphuric acid soln. of silver sulphate becomes brownish-violet or blue when warmed with pyrrhotite. E. F. Anthon, L. T. Wright, and O. Ruff and B. Hirsch also observed that hydrated ferrous sulphide precipitates silver or silver sulphide from soln. of silver nitrate. F. Zambonini, and M. Leo said that the reducing action of ferrous sulphide on soln. of **gold chloride** is stronger than it is with other metal sulphides; the layer of gold produced by pyrrhotite in 24 hrs. is thicker than it is with pyrite in 8 days. R. J. Traill and W. R. McClelland found that pyrrhotite, but not pyrite, dissolves readily in a soln. of **ferric chloride**.

F. Martin and O. Fuchs observed that **calcium sulphate** reacts with ferrous sulphide producing calcium ferrite and sulphur dioxide:  $16\text{FeS} + 23\text{CaSO}_4 = 4\text{Ca}_3\text{Fe}_4\text{O}_9 + 11\text{CaS} + 28\text{SO}_2$ ; and between 920° and 930°, the yield is 8 to 9 per cent. of sulphur dioxide per hour, and at 950°, 13 per cent. A suitable mixture for preparing sulphur dioxide is:  $2\text{FeS} + 4\text{CaSO}_4$ ; with **strontium sulphate**, the most favourable temp. is 1075°; and with **barium sulphate**, 1175° to 1225°. C. Künzel found the reaction with sand in addition, at a red-heat, can be represented:  $3\text{BaSO}_4 + 4\text{SiO}_2 + \text{FeS} = 3\text{BaSiO}_3 + \text{FeSiO}_3 + 4\text{SO}_2$ . E. Schürmann found that a soln. of **zinc sulphate** is completely precipitated by ferrous sulphide; and O. Ruff and B. Hirsch added that after 60 mins' boiling, the precipitate contains 14.3

gram-atoms of Zn, to 0.40 of Fe. H. N. Stokes found that an ammoniacal soln. of **zinc chloride** has no action on precipitated ferrous sulphide at ordinary temp., but in a sealed tube at 160° to 170°, ferrous hydroxide and zinc sulphide are formed—*vide supra*. E. F. Anthon observed that hydrated ferrous sulphide precipitates cadmium sulphide from a soln. of **cadmium sulphate**. F. Feigl and co-workers found that ferrous sulphide reacts with a soln. of **mercuric chloride** forming mercuric sulphide and ferrous chloride; and when a cold, sat., ammoniacal soln. of **mercuric cyanide** is evaporated to dryness with precipitated ferrous sulphide, and afterwards calcined, F. W. Schmidt and R. von der Linde observed that ferric oxide remains. E. Schürmann found that **thallium nitrate** and ferrous sulphide partially precipitate some thallium as sulphide. W. O. Hickok observed no reaction with a soln. of **stannous chloride**. E. F. Anthon observed that hydrated ferrous sulphide, and a soln. of **lead nitrate**, with 15 mins'. boiling, precipitate the lead as sulphide. E. F. Anthon, and E. Schürmann observed no precipitate with soln. of **manganese sulphate**. O. Ruff and B. Hirsch studied the reaction with **nickel and cobalt sulphates**. F. A. Eustis represented the reaction with **ferric chloride** by  $2\text{FeCl}_3 + \text{FeS} = 3\text{FeCl}_2 + \text{S}$ , and said that the reaction is almost complete. E. F. Anthon, E. Schürmann, and O. Ruff and B. Hirsch said that the reaction with ferrous sulphide and soln. of **cobalt nitrate** depends on how long the soln. is boiled; and similarly with soln. of **nickel nitrate**.

Ferrous sulphide unites with other **metal sulphides** to form complex sulphides. F. Warlimont found that **copper sulphide** begins to react with ferrous sulphide when heated in air at 450° to 550° and copper sulphate and ferric oxide are formed. W. Böttger and K. Druschke studied the mutual precipitation of iron and copper sulphides. P. Fischer found that mixtures of ferrous sulphide and **silver sulphide** show a conductivity curve with a maximum and a minimum; and mixtures of ferrous sulphide and **lead sulphide** are non-conducting up to 50 per cent. PbO, and with higher proportions the conductivity rapidly increases. According to E. Diepschlag and E. Horn, the reaction between ferrous sulphide and **ferric oxide** begins at about 500°, and at 800° to 850° the reaction  $\text{FeS} + 10\text{Fe}_2\text{O}_3 = 7\text{Fe}_3\text{O}_4 + \text{SO}_2$  is complete; the reduction of the ferrosic oxide to ferrous oxide begins at about 1100°, and the reaction  $\text{FeS} + 3\text{Fe}_3\text{O}_4 = 10\text{FeO} + \text{SO}_2$  then occurs. The reaction was also studied by L. Wöhler and co-workers, F. Martin and O. Fuchs, L. L. de Koninck, W. F. Hillebrand and H. N. Stokes, and J. H. L. Vogt. F. Warlimont said that **nickel sulphide** is scarcely attacked by ferrous sulphide at 550°.

**Complex salts of ferrous sulphide.**—C. Brunner<sup>19</sup> prepared prismatic, bronze crystals of **sodium ferrous sulphide**,  $\text{Na}_2\text{S} \cdot 2\text{FeS}$ , by calcining a mixture of ferrous oxalate and sodium thiosulphate. H. Freeman observed that when fused with sodium sulphide, iron sulphide forms a complex salt soluble in water. F. Thomas made a few observations on the m.p. of mixtures of ferrous and sodium sulphides, and the results of L. V. Steck and co-workers, for mixtures with over 37 per cent. of ferrous sulphide, are summarized in Fig. 614. The diagram is still incomplete. There is a region between 53 and 73 per cent. iron sulphide in which two liquid phases can form, one being a double compound, probably  $\text{FeS} \cdot \text{Na}_2\text{S}$ , sat. with iron sulphide, and the other being iron sulphide sat. with a double compound, or some-

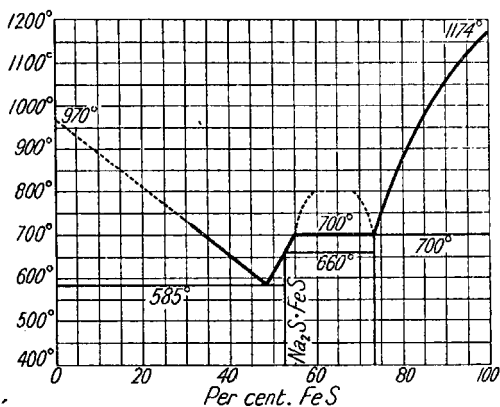


FIG. 614.—Equilibrium Curves for the System:  $\text{Na}_2\text{S}$ - $\text{FeS}$ .



thing similar to it. One true eutectic is found at 46 per cent. of iron sulphide and  $585^{\circ}$ . The m.p. of sodium sulphide has been determined as  $970^{\circ}$ , although its purity was such that the m.p. of pure sodium sulphide can be expected to be slightly higher. According to S. M. Horsch, when hydrogen sulphide is passed over a molten mixture of sodium hydroxide and ferric oxide, **sodium ferrous pentasulphide**,  $\text{FeS} \cdot 4\text{Na}_2\text{S}$ , is produced; the salt dissolves in water, giving a deep emerald-green

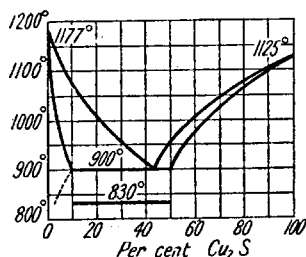


FIG. 615.—Fusion Curves of the System:  $\text{FeS}-\text{Cu}_2\text{S}$ .

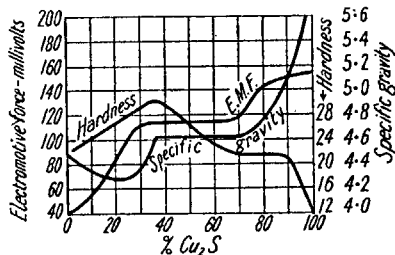


FIG. 616.—Properties of the  $\text{FeS}-\text{Cu}_2\text{S}$  alloys.

soln. Its aq. soln., after dialysis, in the absence of air, retains the two sulphides in the proportion given. A conc. soln. on cooling gives a hydrogel, having the composition  $\text{Na}_2\text{S} \cdot 2\text{FeS}$ , which dissolves in water, giving a black soln., and on adding ammonium chloride to this soln., ferrous sulphide is precipitated. If to this soln., the requisite amount of sodium sulphide is added, it regains the original green colour. R. Schneider found that when potassium ferric sulphide

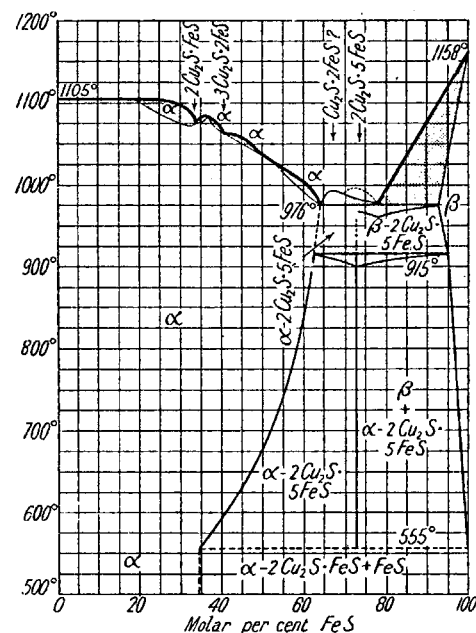


FIG. 617.—Freezing-point Curves of the System:  $\text{Cu}_2\text{S}-\text{FeS}$ .

is heated in hydrogen, black crystals of **potassium ferrous sulphide**,  $\text{K}_2\text{S} \cdot 2\text{FeS}$ , are formed; and K. Preiss obtained needle-like crystals, resembling those of potassium permanganate, by melting together one part of iron filings with ten parts of a mixture of equal proportions of potassium carbonate and sulphur—*vide infra*, complex salts of ferrous sulphide. The products obtained by H. Malfatti may be complex salts of ferric sulphide (*q.v.*), but they have not been definitely established as chemical individuals.

K. Bornemann and F. Schreyer prepared three complexes with copper sulphide by heating mixtures of the two sulphides in an atm. of nitrogen. Their f.p. curve is shown in Fig. 617. P. P. Fedotieff obtained a simple V-curve as illustrated in Fig. 615, showing no evidence of the existence of compounds. The two compounds are only partially miscible in the solid state. O. Reuleaux, and K. Bornemann and H. Schad also made observations on this subject; and H. Tiedemann, and P. P. Fedotieff studied the subject from the point of view of the formation of hair copper. C. B. Carpenter and C. R. Hayward obtained a curve with two branches intersecting at the eutectic at  $995^{\circ}$  and 68 per cent.  $\text{FeS}$ ; solid soln. are formed with limits of

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solubility at 92.5 and 50 per cent. of FeS respectively. Ferrous sulphide melts at 1163° and cuprous sulphide, at 1128°. A transformation occurs in the solid soln. at 950° due to a dimorphic change in the crystal habit of cuprous sulphide. There is a loss of sulphur in the range 15 to 45 per cent. FeS when the mixture is heated above its m.p., and copper is formed. Observations were also made by P. Röntgen, A. Gibb and R. C. Philip, E. Keller, F. H. Edwards, H. O. Hofman and co-workers, A. Baykoff and N. Troutneff, W. Guertler and K. L. Meissner, W. Guertler and O. Reuleaux, C. F. Plattner, C. H. Fulton and I. E. Goodner, J. W. Richards, O. Reuleaux, K. Bornemann and H. Schad, E. L. Larison, E. D. Peters, and F. Frölich. W. Guertler studied the system: Fe-Cu-S. According to G. Tammann and H. Bohner, in the quaternary system:  $\text{Cu}_2\text{S} + \text{Fe} \rightleftharpoons \text{FeS} + 2\text{Cu}$ , at certain concentrations, mixtures of liquid copper and cuprous sulphide and of iron and copper are immiscible, the diagram shows the existence of an area in which three layers are formed instead of two, one of sulphide and two are metallic. Analysis of the layers formed by melting together equivalent amounts of iron and cuprous sulphide shows that the copper and iron are divided practically equally between the metal and sulphide layers. This corresponds to the very small heat of the forward reaction in the above equation. Manganese or aluminium, the sulphides of which have much higher heats of formation than those of copper or iron, can displace the latter two metals almost completely from the molten sulphide layer. F. H. Edwards measured Shore's hardness,  $H$ , the sp. gr., and the e.m.f. of a cell with the alloy and platinum as electrodes and an acid electrolyte. The results are plotted in Fig. 616. Only **cuprous ferrous trisulphide**,  $2\text{Cu}_2\text{S} \cdot \text{FeS}$ , Fig. 617, is stable at all temp. below the f.p. At 915°, **cuprous ferrous heptasulphide**,  $2\text{Cu}_2\text{S} \cdot 5\text{FeS}$ , undergoes a transformation, and between 540° and 570°—say 550°—breaks up into ferrous sulphide and the complex trisulphide; while **cuprous ferrous pentasulphide**,  $3\text{Cu}_2\text{S} \cdot 2\text{FeS}$ , undergoes a change at 180° to 230° forming copper and probably iron disulphides which furnish a solid soln. with the undecomposed compound. P. Ramdohr and O. Oedman described a mineral occurring in minute hexagonal scales at Kaveltorp, Sweden; they called it *vallerite*; and represented it by  $\text{Cu}_2\text{Fe}_4\text{S}_7$ , or  $\text{Cu}_3\text{Fe}_4\text{S}_7$ . L. Cambi and L. Szegö, and R. Schneider described **potassium copper ferric sulphide**,  $\text{K}_2\text{FeCu}_3\text{S}_4$ , which, according to L. Cambi and L. Szegö, has a tetragonal lattice with  $a : c = 1 : 1.182$ . M. Legraye described a **cupric ferrous sulphide**,  $\text{CuS} \cdot 2\text{FeS}$ , or  $\text{CuFe}_2\text{S}_3$ , from the Katanga copper ores, and it was called *orange borrite*. W. Guertler and E. Lüder studied the formation of **silver ferrous sulphide** in the ternary system: Ag-Fe-S—*vide* silver ferric sulphides. W. Guertler and E. Lüder also studied the system: Ag-Cu-Fe-S. V. Nikitin considered *silver pyrites* is a solid soln. of FeS in  $\text{AgFeS}_2$ . J. S. Maclaurin obtained a small yield of **gold ferrous sulphide**,  $\text{Au}_2\text{S} \cdot \text{FeS}$ , by melting together gold and iron in the presence of sulphur.

W. P. Jorissen and B. L. Ongkiehong studied the limits of the reaction between iron, magnesium, and sulphur. K. Friedrich found that no **zinc ferrous sulphide** is formed when the component sulphides are fused together; the f.p. curve, Fig. 618, shows a eutectic at about 1175°, and 5 per cent. of zinc sulphide. The mineral *marmatite*, described by J. B. J. D. Boussingault, has a composition approximating  $3\text{ZnS} \cdot \text{FeS}$ . A. Breithaupt described a variety which he called *christophite*,  $2\text{ZnS} \cdot \text{FeS}$ , from the St. Christophe mine, Breitenbrunn; and J. H. Collins, a similar mineral from St. Agnes, Cornwall. These minerals are to be regarded as ferruginous sphalerites with the ratio  $\text{ZnS} : \text{FeS}$  varying from 5 : 1 to 2 : 1. W. F. de Jong said the X-radiograms correspond rather with mixed crystals than with definite compounds. For sphalerite the lattice parameter  $a = 5.394 \text{ \AA}$ ; for marmatite,  $\text{Zn}_{0.73}(\text{Fe}, \text{Mn})_{0.27}\text{S}$ ,  $a = 5.415 \text{ \AA}$ ; and for christophite,  $\text{Zn}_{0.66}(\text{Fe}, \text{Mn})_{0.34}\text{S}$ ,  $a = 5.420 \text{ \AA}$ . According to F. Ulrich and V. Vesely, the sphalerite from Chólésoff has the composition  $9\text{ZnS} \cdot \text{FeS}$ . For **cadmium ferrous sulphide**, *vide infra*.

W. P. Jorissen and B. L. Ongkiehong studied the limits of the reaction between iron, aluminium, and sulphur. According to M. Houdard, when ferrous sulphide

or pyrites is reduced with aluminium, there is formed **aluminium ferrous sulphide**,  $\text{FeS} \cdot \text{Al}_2\text{S}_3$ . H. Ditz represented the reactions  $2\text{FeS}_2 + 2\text{Al} = \text{Fe} + \text{Al}_2\text{S}_3 \cdot \text{FeS}$ , and  $4\text{FeS} + 2\text{Al} = 3\text{Fe} + \text{Al}_2\text{S}_3 \cdot \text{FeS}$ . J. de Haan observed no formation of a **stannous ferrous sulphide** in his study of the f.p. of the binary system:  $\text{SnS}-\text{FeS}$ , Fig. 619. The system was also studied by E. Kordes. The mineral *stannite*—7.46, 24—is a **cuprous stannic ferrous sulphide**,  $\text{Cu}_2\text{SnFeS}_4$ . It is thought that the crystal lattice is of the chalcopyrite type. T. W. Case observed no change in the electrical resistance of stannite on exposure to light. According to K. Friedrich, **lead ferrous sulphide**

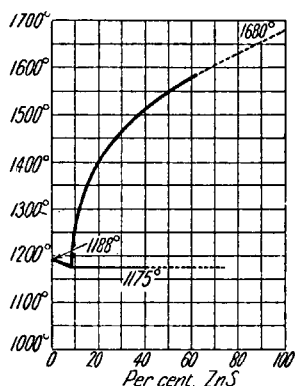


FIG. 618. — Freezing-point Curves of the System:  $\text{ZnS}-\text{FeS}$ .

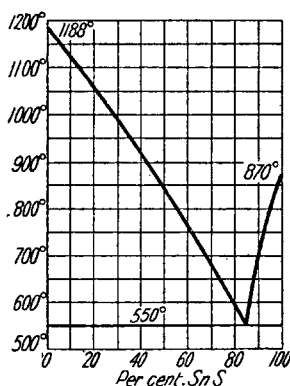


FIG. 619. — Freezing-point Curves of the System:  $\text{SnS}-\text{FeS}$ .

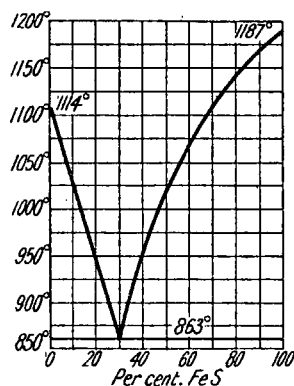


FIG. 620. — Freezing-point Curves of the System:  $\text{PbS}-\text{FeS}$ .

is not formed when the constituent sulphides are melted together. The f.p. curves show a eutectic at  $863^\circ$ , and 70 per cent.  $\text{PbS}$ . E. Kordes, and W. Guertler and W. Leitgeb studied the system  $\text{Fe}-\text{Pb}-\text{S}$ . According to M. Gröger, **ferrous chromic sulphide**,  $\text{Cr}_2\text{S}_3 \cdot \text{FeS}$ , is formed as a black, insoluble compound when a mixture of iron, chromic hydroxide, and sulphur is heated. A black mineral found by J. L. Smith to be associated with troilite in the meteoric stones of Cohahuila, Mexico; Toluca, Mexico; Sevier, Tennessee; and Cranbourne, Australia, was named **daubréelite**—after A. Daubrée. Its composition approximates  $\text{FeS} \cdot \text{Cr}_2\text{S}_3$ . Its sp. gr. is 5.01, and it is not magnetic. S. Meunier synthesized it by treating at a red-heat an alloy of chromium and iron, chromite, or a mixture of ferrous and chromic chlorides, with hydrogen sulphide. Daubréelite was also studied by A. Brezina, A. Brezina and E. Cohen, L. H. Borgström, A. Lacroix, and F. Zambonini. The chromic oxide found by C. U. Shepard in meteorites, and called *schreibersite*, may have been daubréelite. W. Haidinger called it *shepardite*. For the complex **antimony ferrous sulphide**, *vide* the sulphoantimonates.

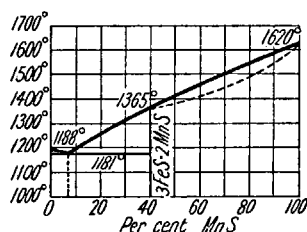


FIG. 621. — Freezing-point Curves of the System:  $\text{FeS}-\text{MnS}$ .

G. Röhl<sup>20</sup> studied the f.p. curves of the system:  $\text{MnS}-\text{FeS}$ , and his results are summarized in Fig. 621. There is a eutectic at  $1181^\circ$  with about 7 per cent. of manganous sulphide. The microscopic evidence indicates that with about 40 per cent. of manganese sulphide, **manganese ferrous pentasulphide**,  $3\text{FeS} \cdot 2\text{MnS}$ , melting at  $1365^\circ$ , is formed. An unlimited series of solid soln. are formed with the dubious compound  $\text{Fe}_3\text{Mn}_2\text{S}_5$  and manganous sulphide. It was not possible to measure the

solidus curve accurately—*vide supra*, the desulphurization of iron by manganese. Z. Shibata found that the two sulphides mix in all proportions in the fused state, and partially in the solid state. There is a eutectic at  $1164^\circ$  and 6.5 per cent. of  $\text{MnS}$ . The binary system:  $\text{FeS}-\text{MnS}$  was studied by D. M. Levy,

and G. Röhl. The results were summarized by C. Benedicks and H. Löfquist, in Fig. 622, on the assumption that no compound is formed; and their reconstruction for the system: Fe-Mn-S, based on the observations of J. E. Stead, A. Ledebur,

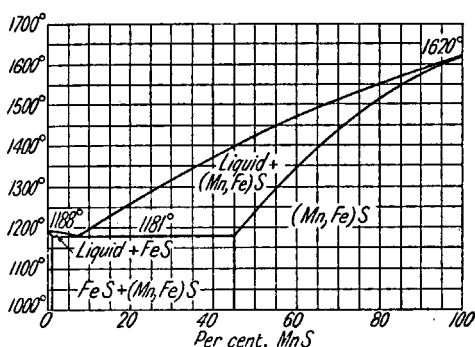


FIG. 622.—The Equilibrium Curves of the Binary System: FeS-MnS.

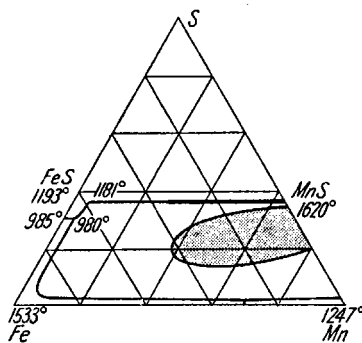


FIG. 623.—The Equilibrium Curves of the Ternary System: Fe-Mn-S.

G. Hilgenstock, H. le Chatelier and A. Ziegler, and E. Schütz, as well as those of M. Levin and G. Tammann, G. Rümelin and K. Fick, H. Esser and P. Oberhoffer, A. Westgren and G. Phragmen, and E. C. Bain on the Fe-Mn system, are indicated in Fig. 623. G. Röhl estimated that solid manganese sulphide dissolves 60 per cent. of FeS, and D. M. Levy, 50 per cent. The solid soln. (Fe,Mn)S is supposed to have the limit 55 per cent. FeS in Fig. 622. Solid ferrous sulphide dissolves very little manganous sulphide. The eutectic FeS-(Mn,Fe)S is at 1181° and 7 per cent. MnS. G. Röhl found that there is a ternary eutectic in the system: Fe-Mn-S, consisting of iron and the two sulphides—4 per cent. MnS. The m.p. of the ternary eutectic is about 980°, a little below 985° the binary eutectic Fe-FeS. There is a region of immiscibility. C. Benedicks and H. Löfquist also constructed space-models of the system. The quadratic diagram, Fig. 624, represents C. Benedicks and H. Löfquist's reconstruction of the quaternary system: MnS-MnO-FeS-FeO. It has not been confirmed by observation; but isolated observations on the system have been reported by C. R. Wohrmann, and M. Matwieff.

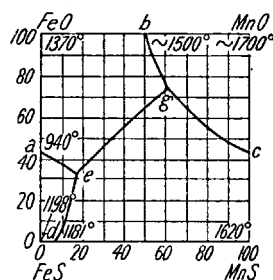


FIG. 624.—The Quaternary System: FeO-MnO-FeS-MnS.

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### § 41. Ferric Sulphide

J. L. Proust,<sup>1</sup> and C. F. Bucholz and A. F. Gehlen reported **ferric sulphide**,  $\text{Fe}_2\text{S}_3$ , to be formed by heating iron or ferrous sulphide with sulphur, in a non-oxidizing atmosphere, until the excess of sulphur is expelled. C. F. Rammelsberg recommended a temp. between  $450^\circ$  and  $500^\circ$ , and R. Scheuer,  $450^\circ$ . Similar results were obtained by L. Gedel. J. J. Berzelius recommended passing hydrogen sulphide over hydrated ferric oxide, at a temp. below  $100^\circ$ , as long as water continues to be formed. E. Brescius, and M. C. Abderhalden observed that if the gas and solid are quite dry, no action occurs under these conditions, and if moisture be present, the conversion of the oxide to ferric sulphide is slow and incomplete. C. F. Rammelsberg could obtain only a mixture of sulphide and oxide by J. J. Berzelius' process, and if a higher temp. be employed pyrrhotite is formed. It is possible that the alleged ferric sulphide prepared by these methods is really a solid soln. of ferrous sulphide and sulphur—*vide supra*. L. J. Proust's product was magnetic; J. J. Berzelius', non-magnetic. R. Juza and W. Biltz did not find this compound formed in the reaction:  $\text{FeS}_2 \rightarrow \text{FeS} + \text{S}$ —*vide infra*.

The question whether the product obtained by the action of hydrogen sulphide on ferric oxide or hydroxide is ferric sulphide or a mixture of ferrous sulphide and sulphur has been the subject of much discussion. A. Wagner, L. Gedel, and E. T. Allen and co-workers regard the product as a mixture of ferrous sulphide and sulphur. G. Gallo observed that ferric sulphide is formed in the action of hydrogen on pyrites at about  $228^\circ$  to  $230^\circ$ . W. Moldenhauer and E. Mischke said that the hydrogen sulphide reduces about two-thirds of the ferric-iron to the ferrous state, and the product is not a mixture of ferrous and ferric sulphides, but rather a compound of the two sulphides. Some consider that a veritable ferric sulphide is formed:  $\text{Fe}_2\text{O}_3 + 3\text{H}_2\text{S} = \text{Fe}_2\text{S}_3 + 3\text{H}_2\text{O}$ . W. Mecklenburg and V. Rodt modified J. J. Berzelius' process by suspending the thoroughly washed, hydrated ferric oxide in water, removing air by a current of carbon dioxide, and passing hydrogen sulphide into the liquid until no more gas is absorbed. After standing 12 hrs., the black precipitate is filtered off, with the exclusion of air, since oxidation readily occurs. It can then be dried over phosphoric oxide in vacuo. G. Weyman, and W. A. Dunkley said that the reactivity of the hydrated oxide depends more on its molecular state than on the amount of moisture present. An oxide which has been heated between  $100^\circ$  and  $600^\circ$  takes up the theoretical amount of gas on cooling; but not so with the oxide heated to  $650^\circ$  or  $800^\circ$ . An oxide with 5 to 8 per cent. water was found by G. H. Gemmel to react best, and this at  $38^\circ$ . J. C. Bell studied

the reactivity of the differently hydrated oxides: and L. T. Wright, P. Hausknecht, R. Scheuer, L. A. Sayce, and T. G. Pearson and P. L. Robinson, the effect of temp. on the absorption of gas. F. Gieseler considered this the best method to use for preparing ferric sulphide. If the oxide is heated during the absorption, some sulphate may be formed. H. Deicke, R. Cox, and E. Brescius showed that an excess of sulphur in the product, assumed to be ferric sulphide, may be due to oxidation by atm. air. The use of ferric oxide in place of lime for absorbing hydrogen sulphide from coal-gas was recommended by E. Heard, and W. R. Bowditch near the beginning of the 19th century. The subject was discussed by G. Anderson, H. Brückner, K. Burkheiser, A. A. Croll, B. Dunglinson and J. M. Gonder, R. Geipert, M. Hempel, F. C. Hills, R. Laming, G. Löwe, F. E. Evans, A. Buhe, and N. H. Schilling.

According to L. T. Wright, **hydrated ferric sulphide**,  $\text{Fe}_2\text{S}_3 \cdot n\text{H}_2\text{O}$ , is formed when hydrated ferric oxide is moistened, or suspended in water, and treated with hydrogen sulphide for several hours—preferably in the absence of air. It was thus prepared by J. J. Berzelius who added that the transformation proceeds at ordinary temp. with a slight evolution of heat, but it is best to employ the heat of a water-bath towards the ends of the operation. The water can be expelled from the hydrate by keeping it in vacuo, preferably over phosphorus pentoxide. The anhydrous sulphide thus obtained is pyrophoric if suddenly exposed to air; otherwise it is quite stable. According to F. Feigl and E. Bäcker, when the washed precipitate of empirical composition  $\text{Fe}_2\text{S}_3$ , formed by precipitation of a tartrate-containing solution of ferric salt with ammonium sulphide, reacts in neutral solution with mercuric and cadmium salts, it behaves as ferrous and ferric sulphide, respectively. This suggests that the substance is a mixture of the valency isomerides  $\text{S} : \text{Fe} \cdot \text{S} : \text{Fe} : \text{S}$  and  $\text{FeS} \cdot \text{FeS}_2$ . H. Krepelka and W. Podrouzek showed that the composition of the precipitate depends on the conditions of precipitation, and similar conditions are valid for the mercaptides of iron. F. Feigl and E. Bäcker found that soln. of ferric salts give ferrous mercaptide with ethyl mercaptan. When, however, the concentration of ferric ion is depressed by addition of tartrate and such a soln. is run slowly into an alcoholic soln. of ethyl mercaptan, **ferric ethyl mercaptide** results. When a solution of ferric chloride is added to a soln. of barium sulphide, or when freshly-precipitated ferric sulphide is treated with a soln. of barium sulphide, a substance approximating to the composition  $\text{BaFe}_2\text{S}_4$  is obtained. This was also prepared by H. Malfatti. The compound reacts with mercuric salts as the original ferric sulphide. It is very unstable and is decomposed by mere washing with water. The compounds described by H. Malfatti are probably mixed sulphides rather than thioferrites. When moist ferric hydroxide is treated with ammonium sulphide, the sulphide formed has the composition  $\text{Fe}_2\text{S}_3$ , whilst that obtained by precipitation from a soln. of ferric salt containing tartrate, has the initial composition  $\text{Fe}_2\text{S}_3 \cdot (\text{NH}_4)_2\text{S}$ .

L. Gedel added that in the purification of coal-gas, the reaction can be represented:  $2\text{Fe}(\text{OH})_3 + 3\text{H}_2\text{S} = \text{Fe}_2\text{S}_3 + 6\text{H}_2\text{O}$ ; the formation of iron disulphide is prevented if traces of ammonia be present. Hydrogen sulphide acts on the dried hydrate  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ , in the presence of hydrochloric acid, to form ferrous sulphide, sulphur, and iron disulphide; while hydrogen sulphide mixed with a little ammonia converts hydrated ferric oxide into ferric sulphide. If air be present along with hydrogen sulphide containing traces of hydrogen chloride, it has no influence on the production of iron disulphide.

As indicated in connection with the preparation of hydrated ferrous sulphide, J. J. Berzelius, and H. N. Stokes showed that hydrated ferric sulphide is formed when a soln. of a ferric salt is added to an excess of ammonium or alkali sulphide soln., but if the alkali sulphide be added to the ferric salt in excess, a mixture of ferrous sulphide and free sulphur is formed. H. N. Stokes showed that if the reaction occurs in the presence of zinc hydroxide, the reaction  $\text{Fe}_2\text{S}_3 + 3\text{Zn}(\text{OH})_2 = 2\text{Fe}(\text{OH})_3 + 3\text{ZnS}$  occurs rapidly in the cold, and instantly on boiling. Alkali

polysulphides precipitate ferrous salts as ferric sulphide. L. A. Sayce found that ferric sulphide is formed by the action of hydrogen sulphide on ferric oxide (*q.v.*). L. Gedel added that a black mixture of ferrous sulphide is formed when ferric chloride is treated with ammonium sulphide in sufficient quantity for all the soln. to remain acidic in virtue of the hydrolysis of the ferric salt; but if enough ammonium sulphide is added to make the soln. of ferric chloride alkaline, the dried precipitate contains ferric sulphide associated with small proportions of ferrous sulphide, sulphur, and iron disulphide. Ferric sulphide is produced when ferrous sulphide is treated with ammonium polysulphide; and if a small proportion of ammonium sulphide be added to an alkaline soln. of a ferric salt—obtained by adding ammonia to a soln. of ferric chloride in tartaric acid—ferric sulphide is formed. T. L. Phipson stated that the hydrate is produced when ferric chloride is added to ammonium sulphide containing a little sodium hypochlorite, or when a ferric salt containing free chlorine or hypochlorite is precipitated by ammonium sulphide. The ammonium sulphide soln. should have acquired by age the ordinary yellow tint. The analysis corresponds with  $\text{Fe}_2\text{S}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ .

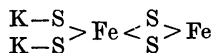
A. Dumansky and A. Yakovléeff prepared **colloidal ferric sulphide** by saturating a hot, 60 per cent. soln. of tartaric acid with washed ferric hydroxide made alkaline with 25 per cent. aq. ammonia, diluting the soln. with 4 to 32 times its vol. of water, and adding an aq. soln. of hydrogen sulphide—0.00369 grm. per c.c. Aq. ammonia hastens coagulation. The sulphide sol is negatively charged, it is easily coagulated by salts, and when warmed it deposits ferric hydroxide and sulphur. J. C. Witt obtained a black amorphous substance by the action of sodium sulphide on ferric oxide, and on washing out the sodium sulphide, there is formed a reversible, green, colloidal soln. with less than 0.07 grm. of iron per litre. J. Casares studied the colloid; and P. Lal and P. B. Ganguly, the action of ultra-violet light on the hydrosol.

The colour of ferric sulphide prepared in a dry way is grey with a yellow tinge which is not so pronounced as in the case of iron disulphide; and J. J. Berzelius added that if it be warmed in vacuo, the yellow colour and lustre become more pronounced. The ferric sulphide prepared by the wet processes is black. T. L. Phipson said that the colour of the hydrate is dark emerald green, and, when collected on a filter, it appears black. The green colour becomes apparent after drying if the powder be ground up with, say, chalk. L. Playfair and J. P. Joule found the sp. gr. to be 4.246; and C. F. Rammelsberg, 4.41. F. Gieseler gave 4.286 for the sp. gr. of ferric sulphide at  $25^\circ/4^\circ$ ; and he calculated 48.5 for the mol. vol., and 11.4 for the at. vol. of the contained sulphur; this gave 25 per cent. for the contraction during the formation of this compound. M. Kimura and M. Takewaki observed that ferric sulphide absorbs ultra-violet rays. J. J. Berzelius said that the sulphide is not magnetic. The dry sulphide is stable in dry air, but when moist, it soon becomes converted into ferric oxide and sulphur. According to V. Rodt, and W. Mecklenburg and V. Rodt, when exposed to air in the presence of alkaline substances, ferric sulphide becomes light yellow owing to the separation of free sulphur, and L. Gedel represented the reaction:  $2\text{Fe}_2\text{S}_3 + 3\text{O}_2 = 2\text{Fe}_2\text{O}_3 + 3\text{S}_2$ . V. Rodt said that no  $\text{FeS}_2$  is formed. The regeneration of the spent ferric oxide, from the hydrogen sulphide purification of coal-gas, by exposure to moist air was discussed by J. C. Bell, A. Buhe, K. Burkheiser, R. Cox, A. A. Croll, H. Deicke, F. E. Evans, E. Heard, P. Hausknecht, F. C. Hills, R. Laming, G. Löwe, W. Mecklenburg and V. Rodt, G. H. Palmers, V. Rodt, E. Schilling, N. H. Schilling, A. Wagner, and L. T. Wright. K. Jellinek and H. Gordon observed that ferric sulphide is almost insoluble in water, and gave  $[\text{Fe}^{+++}]^2[\text{S}^{--}]^3 = 10^{-88}$  for the solubility product. H. N. Stokes found that at  $100^\circ$ , ferric sulphide readily hydrolyzes into ferric hydroxide and hydrogen sulphide. E. Filhol and J. Melliès found that with iodine, ferric sulphide forms ferrous iodide. J. J. Berzelius said that dil. hydrochloric or sulphuric acid acts on ferric sulphide forming hydrogen sulphide, a ferric salt, and iron disulphide; but L. Gedel, and E. Bressius represented the reaction



with hydrochloric acid by the equation:  $\text{Fe}_2\text{S}_3 + 4\text{HCl} = 2\text{FeCl}_2 + 2\text{H}_2\text{S} + \text{S}$ . If some pyrrhotite be present, iron disulphide, ferrous chloride, and hydrogen sulphide are formed. T. L. Phipson stated that ferric sulphide dissolves in hydrochloric acid with effervescence, producing immediately ferric chloride in spite of the abundance of hydrogen sulphide present. According to V. Rodt, and W. Mecklenburg and V. Rodt, if moist hydrated ferric sulphide be exposed to hydrogen sulphide in the absence of air, it is transformed into a mixture of ferrous sulphide and iron disulphide:  $\text{Fe}_2\text{S}_3 = \text{FeS} + \text{FeS}_2$ . This transformation may take place slowly at ordinary temp., but it occupies only a few hours at  $60^\circ$ . T. L. Phipson said that it is appreciably soluble in water containing some ammonia, and separates from soln. as ammonia escapes; it is more readily soluble in water containing free ammonia, it is even more soluble in alcoholic ammonia forming in each case a clear, green soln. which can be filtered. It is only slightly soluble in a mixture of ammonium sulphide and hypochlorite; nor is it more soluble in either of these substances alone. R. F. Weinland and L. Storz observed that with sodium arsenite, ferric sulphide forms ferric hydroxide and hydrogen sulphide; and L. T. Wright, and T. G. Pearson and P. L. Robinson, that a hot soln. of potassium cyanide forms potassium ferrocyanide. E. Jordis and E. Schweizer found that when extracted with carbon disulphide for many days, some sulphur is removed from ferric sulphide; and similarly also with alcohol, or benzene as solvents. L. T. Wright observed that soln. of copper sulphate and silver nitrate are decomposed by ferrous sulphide. H. N. Stokes showed that an ammoniacal soln. of zinc hydroxide reacts:  $\text{Fe}_2\text{S}_3 + 3\text{Zn}(\text{OH})_2 = 2\text{Fe}(\text{OH})_3 + 3\text{ZnS}$ ; a similar result was found by H. Malfatti with ammoniacal cadmium sulphate; but F. Feigl and co-workers represented the reaction:  $\text{Fe}_2\text{S}_3 + 2\text{CdSO}_4 = 2\text{CdS} + \text{S} + 2\text{FeSO}_4$ ; and H. Malfatti obtained ferric hydroxide and lead sulphide with a soln. of lead acetate containing some potassium hydroxide and glycerol. F. Feigl and co-workers found that the reaction with mercuric chloride gives a ferrous salt:  $\text{Fe}_2\text{S}_3 + 2\text{HgCl}_2 = 2\text{HgS} + \text{S} + 2\text{FeCl}_2$ , and this favours the assumption that the formula of ferric sulphide is  $\text{FeS} \cdot \text{FeS}_2$ , otherwise the reaction:  $\text{Fe}_2\text{S}_3 + 3\text{HgCl}_2 = 3\text{HgS} + 2\text{FeCl}_3$  would be anticipated. A number of complex salts occur in nature as minerals or mixtures of minerals.

H. Malfatti showed that there is the probability that when a soln. of ferric chloride is treated with an excess of ammonium sulphide,  $(\text{NH}_4)_2\text{S}$ , **ammonium ferric sulphide**, or **ammonium sulphoferrite**,  $\text{NH}_4\text{FeS}_2$ , is formed. After washing out the ammonium salts, or long standing in water, or warming with water, a green soln. is formed under conditions where ferric sulphide alone is not dissolved. The green soln. is probably the peptized colloid. H. Malfatti similarly obtained **potassium ferric sulphide**, or **potassium sulphoferrite**,  $\text{KFeS}_2$ , by the action of hydrogen sulphide on a mixture of hydrated ferric oxide, and an alcoholic soln. of potassium hydroxide. The black product is decomposed by water to form potassium sulphide and gelatinous, hydrated ferric sulphide. R. Schneider obtained the complex salt,  $\text{KFeS}_2$ , by melting powdered iron with potassium carbonate and sulphur, and leaching the cold product with water. He represented the constitution of the salt by the formula:



The purple-brown, acicular crystals are probably rhombic, and have a sp. gr. of 2.563. If air be excluded, the salt can be heated without decomposition, but in air, potassium sulphate, ferric oxide, and sulphur dioxide are formed. J. Thugutt could not prepare this salt. By heating for 70 hrs. at  $197^\circ$  to  $200^\circ$ , 4 grms. of potassium hydroxide, 3.17 grms. of hydrated ferric oxide, and 40 c.c. of water, sat. with hydrogen sulphide, he obtained a product of the composition  $3\text{K}_2\text{S} \cdot \text{Fe}_2\text{S}_3 \cdot 22\text{H}_2\text{O}$ . R. Schneider's salt is rapidly decomposed by dil. acids with the formation of hydrogen sulphide, and the deposition of sulphur. When heated in hydrogen,

$K_2Fe_2S_3$  is formed. J. Milbauer obtained the salt  $KFeS_2$  by heating ferric oxide with potassium thiocyanate at  $400^\circ$ . The crystals of potassium sulphoferrite,  $KFeS_2$ , were found by H. O'Daniel to be hexagonal, with the axial ratio  $a : c = 1 : 0.3939$ , and the X-radiograms correspond with a lattice having  $a = 13.03$  A., and  $c = 5.40$  A., so that  $a : c = 1 : 0.4144$ . The sp. gr. is 2.66, and if there are eight molecules per unit cell, the calculated sp. gr. is 2.642.

R. Schneider prepared **sodium ferric sulphide**, or **sodium sulphoferrite**,  $NaFeS_2 \cdot 4H_2O$ , by the method he used for the potassium salt. J. Thugutt obtained it by heating for 76 hrs. at  $197^\circ$  to  $200^\circ$  a mixture of 6 grms. of sodium hydroxide, 2.77 grms. of hydrated ferric oxide, and 40 c.c. of water sat. with hydrogen sulphide. H. Fincke studied the action of ferrous sulphide on fused sodium sulphide. According to W. Mecklenburg and V. Rodt, sodium ferric sulphide occurs in the black ash of the Leblanc process for soda, and a convenient method of preparing it is to add a soln. of a ferric salt to an excess of a soln. of sodium sulphide, or to treat a soln. of a ferrous salt with an excess of sodium polysulphide. F. Faktor obtained the anhydrous salt by heating four parts of sodium thiosulphate with one part of iron; it forms dark green, needle-shaped crystals, but loses its crystalline structure on exposure to the air, becoming voluminous, and finally forming a brownish-black powder which gives a dark green soln. in water and evolves hydrogen sulphide when treated with hydrochloric acid. The same amorphous substance may also be prepared by melting sodium thiosulphate with iron at low temp. Sodium iron sulphide is insoluble in water and when heated forms the oxide; by the action of conc. hydrochloric acid, hydrogen sulphide and sulphur are liberated, and when boiled with soln. of potassium cyanide, potassium ferrocyanide is formed. The sodium and potassium salts differ in many ways. Their behaviour towards a soln. of silver nitrate, for instance, is symbolized:  $K_2Fe_2S_4 + 2AgNO_3 = 2KNO_3 + 2AgFeS_2$ ; and  $Na_2Fe_2S_4 + 4AgNO_3 = Ag_4FeS_4 + 2NaNO_3 + Fe(NO_3)_2$ . The  $Fe_2S_4^{--}$  ions may break up into  $Fe^{+} + FeS_4^{---}$  ions, so that the ionization of the complex ferric sulphides may proceed:  $M_2Fe_2S_4 \rightleftharpoons 2M^{+} + Fe_2S_4^{--} \rightleftharpoons 2M^{+} + Fe^{+} + FeS_4^{---}$ . Soln. of the more soluble salt—e.g., the sodium salt—contain more  $FeS_4^{---}$  ions than that of the less soluble salt—e.g., the potassium salt. Hence the different products obtained by the addition of silver nitrate to the aq. soln.

A series of complex **copper ferric sulphides** associated, maybe, with ferrous sulphide, occurs as minerals. For instance:

Chalcopyrite, or copper pyrites	. . . . .	$CuFeS_2$ , or $Cu_2S \cdot Fe_2S_3$
Barnhardite	. . . . .	$Cu_4Fe_2S_5$ , or $2Cu_2S \cdot Fe_2S_3$
Bornite	. . . . .	$Cu_3FeS_3$ , or $3Cu_2S \cdot Fe_2S_3$
Barracanite	. . . . .	$CuFe_2S_4$ , or $CuS \cdot Fe_2S_3$
Chalcopyrrhotite	. . . . .	$CuFe_4S_6$ , or $2FeS \cdot CuS \cdot Fe_2S_3$
Chalmersite (rhombic), cubanite (cubic)	. . . . .	$CuFe_2S_3$ , or $Cu_2S \cdot Fe_4S_5$

There is no general agreement even as to the composition of most of them. Different views may be favoured as to the constitution of these complex salts. P. Groth<sup>2</sup> suggested that they are salts of three **sulphoferric acids**, namely:

Disulphoferric acid, $HFeS_2$ .	Trisulphoferric acid, $H_3FeS_3$ .	Pentasulphodiferric acid, $H_4Fe_2S_5$ .
Chalcopyrite, $Cu'FeS_2$ .	Bornite, $Cu_3'FeS_3$ .	Barnhardite, $Cu_4'Fe_2S_5$ .
Barracanite, $Cu''(FeS_2)_2$ .	Cubanite, $Fe''Cu'FeS_3$ .	
	Chalcopyrrhotite, $(Cu'', Fe'')_3(FeS_3)_2$ .	

The term *χαλκίτης* was used for the copper ore of Cyprus, by Aristotle, about 400 B.C., and apparently also by Dioscorides, in his *De materia medica* (5. 89), in the first century; whilst the term *πυρίτης*, and *pyrites* was also used by Dioscorides, and by Pliny, in his *Historia naturalis* (36. 30), written in the first century of our era. It is also evident that these writers included copper-pyrites under the name *pyrites*. G. Agricola,<sup>3</sup> and C. Gesner distinguished copper-pyrites from ordinary pyrites (*q.v.*) by calling the former *Geekis*, or *Kupferkis*; and

J. F. Henckel said that **chalcopyrite** is a good distinctive name for the ore. The same term was used by F. S. Beudant, and J. G. Wallerius, whilst W. H. Miller proposed the term *townite*—from its occurrence in Huel Towan, Cornwall.

A mineral, more bronze-like than chalcopyrite, was found by A. Breithaupt amongst the copper ores of Plauen, Voigtland, and elsewhere. It was called *homichlin*—from *ομιχλη*, a cloud. It occurs in tetragonal, octahedral crystals, or else massive. Its sp. gr. is 4.472–4.480, and its hardness is 4 to 5. Its composition is close to that of chalcopyrite. It was analyzed by F. Richter. J. D. Dana identified it with barnhardite; C. F. Rammelsberg, with bornite; and G. A. Kenngott, and P. Groth and K. Mieleitner, with chalcopyrite. It may be chalcopyrite partly altered to bornite.

Analyses were reported, in the early days, by R. Chenevix,<sup>4</sup> A. Gueniveau, R. J. Häüy, A. Breithaupt, C. C. von Leonhard, M. V. Hartwall, etc. Other analyses were reported by H. Stölting, P. Jannasch, T. Haege, H. Laspeyres, A. von Kalcinszky, L. Fletcher, A. d'Achiardi, I. Domeyko, J. L. Soubeiran, B. Blount, C. A. Joy, P. Geijer, P. J. Shenon, E. Bechi, D. Forbes, C. D. Pilide, A. Raimondi, J. H. Collins, F. J. Malaguti and J. Durocher, G. T. Prior, A. Lacroix, P. Pilipenko, etc. The results agree with the formula  $\text{CuFeS}_2$  mixed with more or less pyrite. Chalcopyrite sometimes contains gold and silver. A. Dieseldorff, for instance, found the mineral from Wortupa, South Australia, to be comparatively rich in gold. C. W. Dickson observed platinum in a sample from Sudbury. Thallium (*q.v.*) is often present; and C. F. Rammelsberg mentioned the presence of traces of selenium. A. de Gramont discussed the constituents revealed by the spark spectrum.

R. Phillips, and H. Rose represented the composition of the mineral by the formula:  $\text{CuFeS}_2$ ; and H. Rose showed that the assumption that it is constituted as a **cuprous ferric disulphide**, or **cuprous sulphoferrite**,  $\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$ , or  $\text{CuFeS}_2$ , agrees better with the facts than does the assumption made by R. Phillips that it is constituted  $\text{CuS} \cdot \text{FeS}$ . G. Rose, and P. Berthier also adopted this hypothesis, and A. Knop showed that this formula,  $\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$ , is more in accord with the behaviour of the mineral towards hydrochloric acid. C. F. Rammelsberg at first favoured R. Phillips' hypothesis, but later, in view of R. Schneider's synthesis from cuprous chloride, and potassium ferric sulphide, P. Groth regarded it as the cuprous salt of a sulphoferric acid,  $\text{Cu}(\text{FeS}_2)'$ . F. Beijerinck did not favour this hypothesis, but J. Beckenkamp did. T. T. Read, and L. P. Morgan and E. F. Smith titrated a soln. of the mineral with potassium permanganate, and considered that the iron is present in the ferrous, not ferric state, and they suggested that chalcopyrite is a marcasite, with part of the iron replaced by copper. E. C. Sullivan, and H. N. Stokes did not agree. M. Legraye, and A. Laitakarl discussed the formation of copper pyrites.

C. L. Burdick and J. H. Ellis found that the space-lattice of chalcopyrite, Fig. 625, is tetragonal with the axial ratios  $a : b : c = 1 : 1 : 0.985$ . The iron and

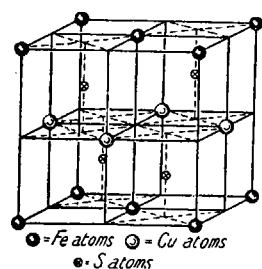


FIG. 625.—Space-Lattice of Chalcopyrite.

copper atoms are located so that they together form a face-centred tetragonal lattice, the planes perpendicular to the tetragonal axis being made up alternately of copper atoms alone and iron atoms alone. The sulphur atoms are located on a similar face-centred lattice with the planes of the sulphur atoms lying midway in all three of the axial directions between the planes of the iron and copper atoms. The subject was also investigated by R. and N. Gross, who regarded chalcopyrite as having the same general character as dolomite. F. Rinne considered magnetite,  $\text{FeFe}_2\text{O}_4$ , and chalcopyrite,  $\text{Cu}_2\text{Fe}_2\text{S}_4$ , to be isometric. L. Pauling and L. O. Brockway found the unit cell had 4 mols. of  $\text{CuFeS}_2$ ; that  $a = 5.24$  Å., and  $c = 10.30$  Å.; the closest distance of copper and sulphur atoms is 2.32 Å., and of the iron and sulphur atoms, 2.20 Å.; and they infer that the atoms have no

fixed valencies, but fluctuate between  $\text{Cu}'\text{Fe}'''\text{S}_2$  and  $\text{Cu}'\text{Fe}''\text{S}_2$ . H. O'Daniel studied the subject.

Chalcopyrite and bornite are probably of magnetic origin. They are widely disseminated minerals which occur in metallic veins and pockets, and in contact zones in gneiss and crystalline schists, and occurrences in serpentized rocks have been noted by B. Lotti,<sup>5</sup> R. Beck and W. von Fircks, and W. H. Weed; in dioritic rocks, by A. Schenck; and in pegmatite, by J. F. Kemp, and J. Catharinet. It occurs as impregnations or replacements in secondary rocks. It is frequently associated with iron pyrites, pyrrhotite, arsenical pyrites, siderite, tetrahedrite, bornite, fahlerz, sphalerite, chalcocite, and sometimes with pentlandite. This subject was discussed by S. G. Lasky, C. Lausen, O. Mügge, P. J. Shenon, A. Sadebeck, O. von Huber, H. W. Turner and A. F. Rogers, K. Schlossmacher, F. Klockmann, H. Schneiderhöhn, M. L. Huggins, W. H. Newhouse, P. Ramdohr, G. M. Schwartz, P. Erimesco, and M. Brinkmann. F. Zambonini inferred that the chalcopyrite of Bocca nel Pigna, Vesuvius, was formed by the action of hydrogen sulphide on soln. of copper and iron chlorides. A. Sadebeck described pseudomorphs of chalcopyrite after fahlerz; P. von Jereméeff, after chalcocite; F. Sandberger, after galena; H. A. Miers, after bournonite; E. Döll, after cuprite; G. N. Maier, and A. Arzruni, after magnetite; H. A. Miers, bismuthinite; and J. R. Blum, after fossils—like ammonites, brachiopods, snails, and fish remains.

J. F. L. Hausmann observed chalcopyrite in the masonry of a roasting furnace at Goslar; A. Reich, in the hearth of a reverberatory furnace at Halsbrücke; A. Reuss, and F. Stolba, in the blast-furnace products near Trautenau; B. von Cotta, and C. W. C. Fuchs, in a furnace of the Muldener Hütte, near Freiberg, etc.; F. Gonnard, in a glass furnace at Lyon; and A. N. Winchell, in a furnace in Butte, Montana. A. Daubrée observed the formation of chalcopyrite, chalcocite, bornite, and tetrahedrite on Roman bronzes exposed to the thermal sulphuretted waters of Bagnères-de-Bigorre, Mer-de-Flines, and Bourbonne-les-Bains; and C. A. de Gouvenain noted that Roman coins exposed to the waters of Bourbon l'Archambault were crusted with chalcopyrite. F. Klockmann also noted the formation of the chalcopyrite in the copper tubes carrying the thermal waters near Pest; whilst E. Chuard observed that bronze implements, from the Swiss lake dwellings, were covered with a thin layer of a kind of stanniferous chalcopyrite.

J. Fournet obtained chalcopyrite by simply fusing a mixture of copper sulphide and pyrite. H. de Sénarmont observed that when a soln. containing ferrous and cuprous chlorides, sodium polysulphide, and an excess of sodium hydrocarbonate is heated to  $250^\circ$ , an amorphous chalcopyrite is formed. C. Doelter gently heated a mixture of copper and ferric oxide in the molar proportions 2 : 1 in a current of hydrogen sulphide, and obtained chalcopyrite. E. G. Zies and co-workers observed that when heated in a sealed tube with a soln. of cupric sulphate, pyrrhotite is converted into chalcopyrite and bornite. R. Schneider agitated a faintly ammoniacal soln. of cuprous chloride, eq. to 0.455 gm.  $\text{Cu}_2\text{O}$ , with a gram of potassium ferric disulphide until the remaining liquid no longer contained copper. Crystals of chalcopyrite were thus obtained, and the mode of preparation shows that the reaction is probably symbolized:  $\text{K}_2\text{S} \cdot \text{Fe}_2\text{S}_3 + \text{Cu}_2\text{Cl}_2 = 2\text{KCl} + \text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$ . This reaction is regarded as a demonstration that the substance with the empirical formula  $\text{CuFeS}_2$  contains cuprous copper and ferric iron, the argument, to be conclusive, requires a demonstration that the cuprous sulphide is not oxidized by the ferric sulphide. S. W. Young and N. P. Moore found that chalcocite in a soln. of potassium sulphide, or in an aq. soln. of hydrogen sulphide, forms a colloidal soln. of copper sulphide which passes into chalcopyrite when in contact with ferrous sulphate, colloidal ferric sulphide or magnetite.

The colour of chalcopyrite is brass-yellow with a tinge of green; and it is often tarnished or iridescent, when it has been called *peacock ore*—this ore occurs in Cornwall. The streak is black, and according to J. L. C. Schroeder van der Kolk,<sup>6</sup> the powder is violet. The microstructure and the optical properties of polished

surfaces were examined by H. Schneiderhöhn. J. B. L. Romé de l'Isle, and R. J. Haiiy thought that the crystals belonged to the cubic system, although J. F. Henckel had previously observed quadratic pyramids which formed equi-angled triangles. A. Breithaupt said that the crystals do not belong to the cubic system, and this was confirmed by C. C. von Leonhard, and R. Phillips. J. Beckenkamp said that the crystals from Arakawa are rhombic pyramids; according to W. Haidinger, the crystals are pseudo-cubic, being really tetragonal, with the axial ratio  $a : c = 1 : 0.98525$ ; V. Goldschmidt gave  $1 : 1.3933$ ; and G. T. Prior,  $1 : 0.9853$ . W. Haidinger's results were confirmed by A. Sadebeck, and N. von Kokscharoff. C. L. Burdick and J. H. Ellis' space-lattice agreed with the ratio  $a : c = 1 : 0.985$ . The mineral may occur massive and compact—a reniform or botryoidal variety, with a smooth brassy appearance, is called *blistered copper ore*. Chalcopyrite may also occur in crystals commonly tetrahedral with the sphenoidal (111)-faces large, dull, or oxidized, and diagonally striated; the  $\bar{1}\bar{1}1$ -faces may be small, brilliant, and neither oxidized nor striated; whilst the scalenohedral and other faces are often prominent, and often striated parallel with the (111)-intersection. The sphenoidal and other faces may be also striated. Observations on the crystals were made by O. Luedecke, J. S. Stevenson, V. Goldschmidt and R. Schröder, P. Groth, B. Mauritz, G. Tschermak, J. W. Gruner, A. Himmelbauer, J. Königsberger, G. Flink, V. Goldschmidt, B. Mauritz, P. P. Pilipenko, V. Dürrfeld, M. Ungemach, A. S. Russell, H. Mayer, T. Haegge, G. Cesaro, G. vom Rath, J. Beckenkamp, L. Souheur, L. Tokody, H. Baumhauer, F. Sandberger, A. Frenzel, C. F. Naumann, J. F. Oebike, R. B. Hare, A. Franzénau, A. Lévy, L. Buchrucker, R. P. Greg and W. G. Lettsom, W. J. Lewis and A. L. Hall, S. L. Penfield, and N. W. and M. J. Buerger. According to L. Fletcher, twinning occurs (i) about the (111)-plane with the composition face a penetration twin which may be perpendicular to (111), and sometimes repeated as a fiveling; (ii) about the twinning plane and composition face (101), often in repeated twins; and (iii) the twinning plane (110), twinning axis  $c$ , and complementary penetration twins; whilst (iv) twinning of pseudo-rhombohedral symmetry is rare. The (201)-cleavage is sometimes distinct, and (001), indistinct. M. J. Buerger, and O. Mügge studied the deformation of crystals by pressure. L. Tokody, Z. Toborffy, and A. Himmelbauer studied the corrosion figures. W. Fackert recommended a mixture of 2.5 vols. nitric acid of sp. gr. 1.2 with 4 vols. hydrochloric acid of sp. gr. 1.19, 10 vols. of water, and a "pinch" of potassium chlorate. P. Ramdohr, W. H. Newhouse, J. W. Gruner, and G. M. Schwartz, investigated **intergrowths** of bornite with stannite, pyrrhotite, cubanite, and chalcocite, and C. Lausen, of chalcopyrite with niccolite.

D. Forbes gave 4.185 for the sp. gr. of chalcopyrite; T. Haegge, 4.301; J. Joly, 4.143; G. T. Prior, 4.170; A. Lacroix, 4.100; P. P. Pilipenko, 4.120; E. Madelung and R. Fuchs, 4.1806; J. Beckenkamp, 4.12 to 4.17; J. Samojloff, 4.21; and M. von Schwarz, 4.1 to 4.3. C. Doelter found the artificial crystals to have the sp. gr. 4.196; and R. Schneider, 3.6 at  $15^\circ$ ; while C. L. Burdick and J. H. Ellis calculated from the space-lattice values, Fig. 625, 4.24. E. H. Kraus and J. P. Goldsberry gave 4.2 for the sp. gr., 43.705 for the mol. vol., and for the topic axial ratios  $\chi : \psi : \omega = 3.5407 : 3.5407 : 3.4897$ . W. H. Goodchild studied the mol. vol., and J. J. Saslawsky calculated the vol. contraction which occurs in the formation of chalcopyrite. The hardness of chalcopyrite is 3.5 to 4.0; C. Doelter gave for the artificial crystals, 3 to 4. O. Mügge, and M. J. Buerger studied the plastic deformation of chalcopyrite. E. Madelung and R. Fuchs gave for the compressibility 0.05128 megabars per sq. cm. F. E. Neumann gave 0.1297 to 0.1282 for the sp. heat of chalcopyrite; P. E. W. Oeberg, 0.1291 between  $14^\circ$  and  $99^\circ$ ; J. Joly, 0.12708 to 0.12717 between  $12^\circ$  and  $100^\circ$ ; and A. Sella, 0.1278. J. Joly gave  $470^\circ$  for the m.p., whatever that may mean. L. H. Borgström gave  $620^\circ$  for the dissociation temp. A. de Gramont examined the spark spectrum; A. Pochettino, the cathodoluminescence; and G. Greenwood and D. Tombouljan,

the piezoelectricity. F. Beijerinck, and R. G. Harvey said that the electric conductivity of chalcopyrite is good, and changes with temp; H. Löwy gave  $5 \times 10^{13}$  c.g.s. units. A. Abt measured the electrical resistance of chalcopyrite; and T. W. Case observed no change in the resistance on exposure to light. For the observations of W. G. Hankel, E. Becquerel, R. Bunsen, A. Abt, and J. Stefan on the thermoelectric properties—*vide infra*, pyrite. W. Skey observed that in a soln. of sodium chloride, chalcopyrite is electronegative to silver. I. Bernfeld found that if used as anode in an acid soln., the copper passes into soln. and the sulphur remains behind, or, if the current density is high, it is oxidized. In alkaline soln., as anode, cupric hydroxide is formed and the sulphur is oxidized, and when used as cathode, a copper slime remains behind. E. F. Smith noted that the sulphur is oxidized if the powdered mineral be electrolyzed in molten potassium hydroxide with a nickel dish as anode. K. Fischbeck studied the electrolytic reduction of  $\text{CuFeS}_2$ . E. T. Wherry found that chalcopyrite is a fair radiodetector; this subject was also discussed by C. Tissot and F. Pellin, H. S. Roberts and L. H. Adams, and W. Ogawa. W. Ogawa studied the thermoelectric properties of chalcopyrite and a current of  $10,500\mu$  volt flows from the mineral to the copper at the hot junction. W. R. Crane gave  $127 \times 10^{-6}$  for the magnetic susceptibility.

According to P. Berthier, and C. F. Rammelsberg, when chalcopyrite is heated out of contact with air, about a quarter of the sulphur is given off:  $2\text{CuFeS}_2 = \text{Cu}_2\text{S} + 2\text{FeS} + \text{S}$ . According to F. Beijerinck, when chalcopyrite is heated out of contact with air, sulphur is given off, and, added F. Frölich, the mineral becomes more soluble in dil. acids. F. Thomas said that for the complete removal of the sulphur, the presence of some gangue minerals are necessary, and M. de K. Thompson, that the copper passes into cupric oxide. A. Mourlot found that about 10 per cent. sulphur remained after the mineral had been heated ten minutes in the electric arc furnace. R. Schneider found that at dull redness, 12.5 per cent. of sulphur is lost in an atm. of carbon dioxide, and 25 per cent. in an atm. of hydrogen.

The tarnishing of the mineral on exposure to air has been indicated above. The transformation of chalcopyrite into malachite and azurite where the mineral is exposed to carbonated waters, and also its transformation into chalcocite,  $\text{Cu}_2\text{S}$ , and covellite,  $\text{CuS}$ , have been frequently observed. The oxidation of chalcopyrite was studied by S. H. Emmens, H. Saito, W. H. Emmons, C. R. van Hise, R. C. Wells, and V. H. Gottschalk and H. A. Buehler—*vide infra*, iron pyrites. In nature there are various reactions associated with the action of cupric salt soln., say cupric sulphate, formed by the oxidation of ores in the upper levels; and various copper minerals are convertible one into the other. In illustration, E. G. Zies and co-workers found that by the action of soln. of cupric sulphate, heated in sealed tubes, chalcopyrite was converted into covellite and then to chalcocite; and P. von Jereméeff observed at a locality in the Altai Mts., every stage of transition from chalcopyrite to chalcocite. K. Schlossmacher observed the transformation of bornite into chalcopyrite; and H. A. Miers, and M. Brinkmann, the reverse change:  $\text{Cu}_3\text{FeS}_3 + \text{Fe}_2\text{S}_3 = 3\text{CuFeS}_2$ ; E. Döll reported pseudomorphs of pyrite after chalcopyrite; T. Wada, of copper after chalcopyrite; and F. A. Genth, of hisingerite after chalcopyrite. J. W. Mellor found that when the powdered (200's lawn) mineral is heated, while a current of air is passed over the surface, the percentage losses of the contained sulphur when the mineral is heated 2 to 3 hrs. at the given temp., are those indicated in Fig. 626. F. Foreman observed that when chalcopyrite is heated in a sealed tube:

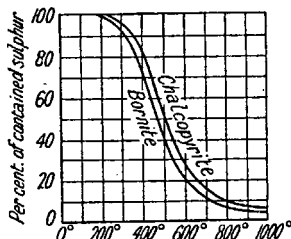


FIG. 626.—Loss of Sulphur when the Minerals are Heated in a Current of Air.

SOLVENT	DISSOLVED	100°	150°	250°	310°	parts per million	
Water	{Fe . . . . .	2.0	0.0	0.40	8.2	,,	,,
	{Cu eq. H <sub>2</sub> S . . . . .	—	0.00	85.20	120.7		
0.1N-NaHCO <sub>3</sub>	{Fe . . . . .	210° 0.00	250° 0.00	275° 5.0	310° 9.8	,,	,,
	{Cu eq. H <sub>2</sub> S . . . . .	—	67.4	114.4	356.0		
0.1N-Na <sub>2</sub> S	{Fe . . . . .	0.00	0.00	0.00	3.0	,,	,,
	{Cu eq. H <sub>2</sub> S . . . . .	35.2	45.7	171.6	228.0		

H. Freundlich and co-workers studied the adsorption of water. C. A. Burghardt found that when chalcopyrite is fused with ammonium nitrate, reddish-brown ferric oxide is formed. S. W. Parr found that the sulphur is all oxidized by the action of molten sodium dioxide; J. Matuschek, by fused potassium nitrate; and C. Boucher, by a mixture of sodium persulphate and ammonium nitrate. R. Schneider said that it is not attacked by hot or cold water. According to C. Doelter, water alone dissolves 0.1660 per cent. of the iron in the chalcopyrite employed. J. Lemberg found that alkaline bromine-water colours the mineral bronze-brown and forms copper and ferric oxides. E. Schäfer said that the mineral is slowly attacked by chlorine at ordinary temp., but at a higher temp. the action is quicker; bromine acts more slowly than chlorine. H. N. Stokes observed that chalcopyrite when exposed to bromine vapour for half a minute, and then to hydrogen sulphide gas, is blackened, whereas iron sulphides remain bright. R. Schneider found that dil. hydrochloric acid has no action, but the hot, conc. acid attacks it vigorously without all the iron passing into soln. A. Knop observed that hydrochloric acid extracts the iron as oxide leaving behind most of the copper—no hydrogen is given off. According to F. Beijerinck, hydrochloric acid slowly attacks chalcopyrite forming covellite. E. E. and I. W. Wark observed the effect of sulpho-compounds on the flotation of the mineral. E. F. Smith said that chalcopyrite is decomposed by sulphur monochloride at 140°, and S. W. Young and N. P. Moore showed the action of soln. of alkali sulphides to be very small. A. Himmelbauer observed the corrosion figures with warm sodium hydroxide soln., and J. Lemberg observed that the boiling lye makes the surfaces of the crystals matt. T. T. Read found that sulphurous acid extracts the iron as ferrous sulphate. A. Himmelbauer did not obtain corrosion figures with sulphuric acid, but Z. Toborffy did. S. W. Young and N. P. Moore observed that a soln. of 0.1N-H<sub>2</sub>SO<sub>4</sub> along with hydrogen sulphide, becomes turbid. R. Schneider found that the mineral is not attacked by dil. alkali lye, or by dil. aq. ammonia. He also found that cold nitric acid of sp. gr. 1.2 has no action, but the mineral dissolves in the hot acid, forming a green soln. with the separation of sulphur; and Z. Toborffy studied the corrosion figures obtained with nitric acid. Aqua regia is the best solvent for chalcopyrite. E. Wilke-Dörfurt and E. A. Wolf opened the mineral for analysis by heating it in the vapour of iodine trichloride. O. Gasparini found that the mineral is energetically oxidized in the presence of nitric acid undergoing electrolysis. J. Lemberg observed that chalcopyrite is not soluble in a boiling soln. of potassium cyanide; he also showed that a soln. of potassium ferrocyanide in acetic acid gradually forms a film of brown copper ferrocyanide which later changes into prussian blue. K. B. Rogers showed that the heated mineral is decomposed by the vapour of carbon tetrachloride. W. O. Hickok observed that chalcopyrite is not acted on by a soln. of stannous chloride. H. N. Stokes found that when a mineral is treated with a soln. of ferric sulphate—*vide infra*, pyrite—bornite can be distinguished from chalcopyrite even when the proportion of copper is less than 3 per cent. A sulphuric acid soln. of silver sulphate at 50°, is coloured reddish-violet by chalcopyrite. Nascent hydrogen from zinc and sulphuric acid was found by F. Beijerinck to develop hydrogen sulphide; if the point of an electrode in an electrolytic current is placed on a polished section of chalcopyrite, a black film appears whilst pyrite and pyrrohotite do not change their appearance. F. P. Treadwell found that if the mineral is heated to dull redness with *ferrum reductum*, in an atm.

of carbon dioxide, ferrous sulphide is formed. T. T. Read observed that if placed in a soln. of copper sulphate, the chalcopyrite becomes richer in copper sulphide. F. Thomas observed that a soln. of ferric sulphate decomposes the mineral slowly, and if powdered rapidly, as observed by F. Thomas, and M. de K. Thompson, the decomposition is faster after an oxidizing roast at  $450^{\circ}$ – $480^{\circ}$ . J. B. Cammerer showed that a soln. of 4 mols of ferric chloride when heated with a mol of finely powdered chalcopyrite, yields 5 mols of ferrous chloride, a mol of cupric chloride, and 2 gram-atoms of sulphur. F. W. Schmidt found that chalcopyrite is decomposed by an ammoniacal soln. of mercuric cyanide; and P. V. Gladkoff, that chalcopyrite rapidly precipitates gold from a dil. soln. of gold chloride. A. K. Burn discussed the flotation of the ore in sea-water, and A. M. Gaudin and W. D. Wilkinson, flotation in the presence of dioxanthogen.

The mineral **barnhardite** was found by F. A. Genth<sup>7</sup> on D. Barnhardt's land, Cabarrus Co., North Carolina, and it has been reported from a few other localities. Analyses presented by F. A. Genth, N. S. Higgins, and F. von Dieffenbach agree approximately with **cuprous ferric pentasulphide**,  $\text{Cu}_4\text{Fe}_2\text{S}_5$ , or  $2\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$ . The mineral occurs in bronze-yellow compact masses. It tarnishes easily on exposure to air. Its sp. gr. is 4.521, and its hardness 3.5. E. H. Kraus and J. P. Goldsberry gave 4.521 for the sp. gr.; 38.806 for the mol. vol., and for the topic axial ratios  $\chi : \psi : \omega = 3.3856 : 3.3856 : 3.3856$ . It may be chalcopyrite partly altered to chalcocite. **Cuprous ferrous stannic sulphide**,  $\text{Cu}_2\text{S} \cdot \text{FeS} \cdot \text{SnS}_2$ , was discussed in connection with tin—7. 76, 24.

In 1725, J. F. Henckel<sup>8</sup> referred to a mineral which he called *Kupfer-lazul*; J. G. Wallerius applied several terms to the brown or violet copper ore, or *cuprum sulfure et ferro mineralisatum*; A. Cronstedt called it *Koppar-lazur* or *miner acupri lazurea*; A. G. Werner, *Buntkupfererz*; R. Kirwan, *purple copper ore*; and R. J. Haüy, *cuvre pyriteux hépatique*. Several other names have been proposed; F. S. Beudant, *phillipsite*—after W. Phillips—but the term was already in use for an aluminosilicate; E. F. Glocker, *poikilopyrite*—from *ποικίλος*, variegated; A. Breithaupt, *poikilite*, and also *Buntkupferkies*; W. Haidinger, *bornite*—after I. Eques a Born; J. D. Dana, *erubescite*—from *erubescere*, to redden; and C. W. Blomstrand, *chalcomiklite*.

A massive mineral resembling bornite was described by C. F. Rammelsberg.<sup>9</sup> It came from Guanasevi, Mexico; its sp. gr. ranged from 5.19 to 5.24, and its hardness was 3. The mineral was called *castillite*, and its composition was represented by the formula  $(\text{Cu}, \text{Ag})_2\text{S} \cdot 2(\text{Cu}, \text{Pb}, \text{Au}, \text{Fe})\text{S}$ , but, as emphasized by J. D. Dana, and G. Kalb, it is probably an impure bornite. R. Pearce observed a related mineral in Butte, Montana.

Analyses were reported by the early workers, M. H. Klaproth,<sup>10</sup> W. Hisinger, R. Brandes, J. J. Berzelius, C. F. Plattner, P. Berthier, C. Staaf, A. Chodneff, W. and R. Phillips, C. Bergemann, and T. Bodemann; and by the later workers, C. F. Rammelsberg, F. Sandberger, F. Katzer, L. Mrazek, G. A. Kenngott, C. Mène, L. L. de Koninck, W. I. Macadam, P. T. Cleve, D. Forbes, I. Domeyko, M. Böcking, A. Hilger and E. von Gerichten, E. von Bibra, B. J. Harrington, A. d'Achiardi, J. D. Dana, H. F. Collins, E. H. Kraus and J. P. Goldsberry, etc. J. J. Berzelius, W. Hisinger, and W. and R. Phillips concluded from their analyses that the mineral is a complex of  $2\text{Cu}_2\text{S} \cdot \text{FeS}$ ; while C. F. Plattner regarded it as a complex **cuprous ferric trisulphide**,  $3\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$ , i.e.  $\text{Cu}_3\text{FeS}_3$ , which C. F. Rammelsberg represented by  $\text{Cu}_2\text{S} \cdot \text{CuS} \cdot \text{FeS}$ . Actually, as emphasized by C. F. Rammelsberg, the analyses extend over a considerable range—the copper being 45 to 70 per cent., and the iron, 6.5 to 15 per cent. As F. von Schaffgotsch showed, quite a number of different formulæ might be defended as giving the best representative value ranging from  $\text{Cu}_2\text{S} : \text{Fe}_2\text{S}_3 = 3 : 1$  to  $9 : 1$ . G. Nordenström, C. F. Rammelsberg, and P. Groth favoured  $3\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$ ; and P. T. Cleve, E. T. Allen, and B. J. Harrington,  $5\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$ ; and E. H. Kraus and J. P. Goldsberry gave formulæ  $\text{Cu}_6\text{Fe}_2\text{S}_6$ ,  $\text{Cu}_8\text{Fe}_2\text{S}_7$ , etc., up to  $\text{Cu}_{76}\text{Fe}_2\text{S}_{41}$ , where the minerals are represented by the general formula:  $\text{Cu}_n\text{Fe}_2\text{S}_{\frac{n}{2}+3}$ . H. Baumhauer proved by microscopic observations that



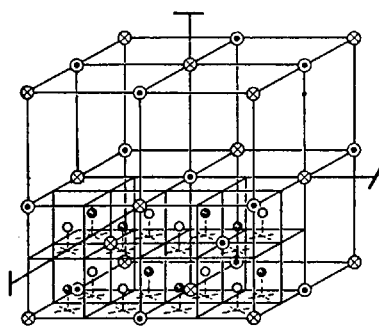
the bornite is particularly liable to contain admixtures—principally chalcocite. J. C. Ray showed that bornite is relatively unstable and readily passes into chalcocite and chalcopyrite with water in sealed bombs at  $100^{\circ}$  to  $175^{\circ}$ . A. F. Rogers suggested that the variation in other cases is due to the existence of solid soln. of  $\text{Cu}_2\text{S}$  in  $\text{CuFeS}_2$ .

The discussion on the formation of chalcopyrite in nature applies to a large extent to bornite, for both minerals are primary constituents from which many other copper minerals are derived. Both minerals indeed frequently occur together. The observations of B. Lotti, R. Beck and W. von Fircks, A. Schenck, J. F. Kemp, S. G. Lasky, W. H. Weed, J. Catharinet, H. W. Turner and A. F. Rogers, and P. von Jereméeff on the occurrence of chalcopyrite in serpentized, dioritic, and pegmatitic rocks apply also to bornite, and agree with the assumption that bornite is of magmatic origin. The occurrence of bornite has been also discussed by A. Frenzel, W. Lindgren, C. Klein, A. F. Rogers, H. Schneiderhöhn, R. H. Sales, E. Weinschenk, P. Geijer, C. Baret, F. B. Laney, P. Krusch, F. Beyschlag, T. L. Walker, K. Schlossmacher, and R. M. Overbeck. Pseudomorphs of bornite after chalcocite and chalcopyrite have been observed, and discussed by C. C. von Leonhard, F. P. Mennel, and K. Schlossmacher. G. Gilbert discussed what he called the antipathy of bornite for pyrrhotite, because he believed that the minerals are mutually exclusive, and if a specimen of one mineral is found, the other will be absent.

A. Reuss observed crystals of bornite in the masonry of a blast-furnace at Trautenau, Bohemia; F. N. Guild, in cavities in the masonry of a smelter at Miami, Arizona; and A. N. Winchell, in a furnace at Butte, Montana. A. Lacroix, and A. Daubrée observed crystals of bornite occur on Roman bronze coins and bronzes which were exposed to the waters of the thermal springs at Bourbonne-les-Bains.

M. Böcking obtained a product resembling bornite by melting, under a layer of sodium chloride, a mixture of 36 grms. of copper, 10 grms. of iron, and sulphur; and F. Marigny, under a layer of borax, a mixture of 20 parts of pyrites, 45 parts of copper, and 20 parts of sulphur. C. Doelter obtained bornite by heating a mixture of different proportions of cuprous, cupric, and ferric oxides in hydrogen sulphide at  $100^{\circ}$  to  $200^{\circ}$ . He thus obtained cubic crystals of  $\text{Cu}_3\text{FeS}_3$ , and with other mixtures, products like  $\text{Cu}_9\text{Fe}_4\text{S}_{10}$ , and  $\text{Cu}_4\text{FeS}_7$ . E. G. Zies and co-workers found pyrrhotite passes into chalcopyrite and probably bornite when it is heated in a sealed tube with a soln. of copper sulphate.

The colour of bornite ranges between copper-red and pinchbeck-brown on a freshly-fractured surface, but the surface quickly tarnishes and appears iridescent.



• = S; ○ = Cu; ⊙ = Cu; ⊗ = Fe  
— = twofold axis

FIG. 627.—The Unit Cubic Cell of Bornite.

Some of the names proposed for the mineral refer to the lustre of the tarnish; and other names, like *peacock ore*, and *horse-flesh ore*, are miners' names suggested by the colour of the mineral. The streak is pale greyish-black, and J. L. C. Schroeder van der Kolk found that the colour of the streak or powder varies with different specimens. Bornite may occur massive with a granular or compact structure; and, as shown by C. C. von Leonhard, and W. Phillips, it occurs in cubic crystals whose habit may be cubic with the faces rough or curved. F. Mohs suggested that the crystals are rhombohedral with an angle of  $95^{\circ}$ , but W. Haidinger showed that the crystals are really cubic, and he compared the effects of twinning of bornite

with that of fluorite. The crystals were also described by A. Breithaupt, L. Buchrucker, A. Lévy, J. D. Dana, etc. Twinning may occur about the (111)-plane, and there may be penetration twinning hexagonal in form. There are traces

of cleavage on the (111)-face. P. F. Kerr, and W. de Jong made observations on the **X-radiogram** of bornite,  $\text{Cu}_5\text{FeS}_4$ . The unit cubic cell is illustrated by Fig. 627. According to J. W. Gruner's summary, of the 40 copper atoms in the unit cell, 32 are cuprous and 8 are cupric. The 32 sulphur atoms occupy the position of oxygen in magnetite, and form a tetrahedral network of face-centred, close-packed particles. The 32 cuprous atoms are arranged in the same manner, and their tetrahedra bear the same relationship to those of the S-atoms, that a positive tetrahedron does to a negative one. There is a small, negligible discrepancy of less than 3 per cent. of the parameter of the cuprous atom. The structure of these 64 atoms closely resembles that of PbS (sodium chloride type). The eight cupric atoms, and eight ferrous atoms are placed in the centres of some of the tetrahedra of sulphur and cuprous atoms. The variable composition of bornite between  $\text{Cu}_6\text{Fe}_2\text{S}_8$  and  $\text{Cu}_{18}\text{Fe}_2\text{S}_{12}$  is the result of an isomorphous replacement of ferrous by cupric atoms and *vice versa*. These two types of atoms have very similar positions, being comparable with positive and negative tetrahedra. Partial replacement should therefore be common. H. Schneiderhöhn studied the microstructure of polished surfaces; J. W. Gruner, intergrowths with chalcopyrite and chalcocite; P. Geijer, corrosion figures with nitric and hydrochloric acids, and soln. of potassium cyanide, and W. Fackert used the corrosive liquid recommended above for chalcopyrite. G. M. Schwartz studied intergrowths with chalcocite.

F. Sandberger gave 5·7 for the sp. gr.; F. Katzer, 4·91; C. Staaf, 4·988; P. T. Cleve, 4·81 to 5·425; C. F. Rammelsberg, 5·03; and E. T. Allen, 5·037 to 5·103 at 25°/25°. The sp. gr., of course, varies with the composition. E. H. Kraus and J. P. Goldsberry gave for the sp. gr. the mol. vol.:

	$\text{Cu}_6\text{Fe}_2\text{S}_8$	$\text{Cu}_{10}\text{Fe}_2\text{S}_8$	$\text{Cu}_{12}\text{Fe}_2\text{S}_9$	$\text{Cu}_{12}\text{Fe}_2\text{S}_{10}$
Sp. gr. . . . .	4·9	5·072	5·086	5·248
Mol. vol. . . . .	34·977	32·989	32·672	31·516

The topic axial ratios  $\chi : \psi : \omega$  were all 3·2704 for  $\text{Cu}_6\text{Fe}_2\text{S}_8$ ; 3·2072, for  $\text{Cu}_{10}\text{Fe}_2\text{S}_8$ ; 3·1950 for  $\text{Cu}_{12}\text{Fe}_2\text{S}_9$ ; and 3·1587 for  $\text{Cu}_{14}\text{Fe}_2\text{S}_{10}$ . J. J. Saslawsky calculated the contraction which occurs in the formation of bornite. The hardness of the mineral is 3. A. Sella found the sp. ht. to be 0·1195. J. Joly gave 430° for the m.p., whatever that may mean. A. de Gramont examined the spark spectrum. R. D. Harvey, and F. Beijerinck showed that the electric conductivity of the mineral is good, and increases with rise of temp.; and T. W. Case observed no change in the resistance on exposure to light. E. T. Wherry found that bornite is a poor radio-detector; H. S. Roberts and L. H. Adams discussed the use of bornite as a radio-detector, and W. Ogawa found that the thermoelectric force of bornite against copper is 6650 $\mu$  volt, and the current flows from copper to the mineral at the hot junction.

J. F. L. Hausmann found that while bornite is readily oxidized in moist air, it is not oxidized in dry air. J. W. Mellor's observations on the oxidation of the powdered mineral in a limited supply of air are indicated in Fig. 626. Bornite oxidizes faster than chalcopyrite. F. Carmichael observed that 0·01 per cent. of powdered bornite is oxidized when the powdered mineral is agitated for 13 days with water and oxygen. S. H. Emmens, W. H. Emmons, R. C. Wells, C. R. van Hise, and V. H. Gottschalk and H. A. Buehler studied this subject—*vide infra*, iron pyrites. R. Blanchard and P. F. Boswell discussed the formation of limonite from bornite. J. Lemberg observed that with alkaline bromine-water, bornite acquires a brownish-black film of copper and ferric oxides. J. Lemberg found that bornite is soluble in conc. hydrochloric or nitric acid with the separation of sulphur, and in a boiling soln. of potassium cyanide—pyrite, chalcopyrite, magnetite, and löllingite are not soluble in that menstruum. E. E. and I. W. Wark studied the effect of sulpho-compounds on the flotation of the mineral. S. W. Young and N. P. Moore found that bornite is stable in a 0·1N- $\text{H}_2\text{SO}_4$  sat. with hydrogen sulphide; and with an alkaline soln. of potassium sulphide, or water sat. with hydrogen sulphide, bornite is peptized, and the colloidal soln. forms chalcocite, and chalc-

pyrite. J. D. Sullivan found that bornite is soluble in soln. of ferric sulphate. J. Lemberg said that with potassium ferrocyanide and hydrochloric acid, brown copper ferrocyanide and prussian blue are formed—*vide supra*, chalcopyrite.

C. F. Rammelsberg<sup>11</sup> applied the term *cupropyrrite* to a mixture of chalcopyrite and pyrite; it had the general properties of cubanite—*vide infra*—but differed from it in chemical composition and sp. gr. C. H. Scheidhauer represented it by the formula:  $\text{CuFe}_2\text{S}_3$ , or  $\text{Cu}_2\text{Fe}_4\text{S}_6$ , and proposed to call it **barracanite** in allusion to its occurrence at Barracanao, Cuba. Analyses were reported by C. H. Scheidhauer, and J. D. Dana. P. Groth and K. Mieleitner considered it to be **cupric ferric disulphide**,  $\text{Cu}(\text{FeS}_2)_2$ . The crystals belong to the cubic system; and the sp. gr. given by J. D. Dana is 4·17 to 4·18.

A. Breithaupt applied the term *cuban*, and E. J. Chapman **cubanite** to a bronze- or brass-yellow, massive mineral from Barracanao, Cuba. Analyses reported by C. H. Scheidhauer, P. T. Cleve, and R. Schneider correspond with **cuprous ferric hexasulphide**,  $\text{Cu}_2\text{Fe}_4\text{S}_6$ , or  $\text{Cu}_2\text{S} \cdot \text{Fe}_4\text{S}_5$ , or  $\text{Cu}_2\text{S} \cdot \text{FeS}_2 \cdot 3\text{FeS}$ . C. F. Rammelsberg, and G. A. Kenngott regarded cubanite as a variety of bornite with a high proportion of iron sulphide. R. Schneider gave the formula  $\text{CuFeS}_4$  for cubanite. C. F. Rammelsberg based his formula on the reaction between cubanite and silver nitrate which is symbolized:  $\text{Cu}_2\text{S} \cdot 3\text{FeS} \cdot \text{FeS}_2 + 10\text{AgNO}_3 = 4\text{Ag}_2\text{S} \cdot \text{FeS}_2 + 2\text{Cu}(\text{NO}_3)_2 + 3\text{Fe}(\text{NO}_3)_2 + 2\text{Ag}$ . The crystals belong to the cubic system; and the sp. gr. is 4·026 to 4·042, and the hardness 3·5. H. E. Merwin and co-workers argued that cubanite and chalmersite are really the same minerals, both rhombic; and P. Geijer, that cubanite and chalcopyrite are the same. J. W. Gruner, G. W. Schwarz, P. Ramdohr, A. Bibolino, N. W. and M. J. Buerger, and W. H. Newhouse discussed intergrowths with chalcopyrite.

E. Hussak<sup>12</sup> described a brass- or bronze-yellow mineral from Minas Geraes, Brazil, which was called **chalmersite**—after G. Chalmers. According to C. Palache, analyses reported by G. Kalb and M. Bendig, and E. T. Allen, corresponded with  $\text{Cu}_2\text{S} \cdot \text{Fe}_4\text{S}_5$ , or  $\text{CuFe}_2\text{S}_3$ , whilst E. Hussak gave  $\text{CuFe}_2\text{S}_4$ , or  $\text{Cu}_2\text{S} \cdot \text{Fe}_4\text{S}_7$ . P. Groth and K. Mieleitner regarded chalmersite as a sulphosalt,  $\text{FeCu}(\text{FeS}_3)$ . The rhombic crystals were found by C. Palache to have the axial ratios  $a : b : c = 0·5725 : 1 : 0·9637$ ; C. Hlawatsch gave  $0·5822 : 1 : 0·5611$ ; and E. Hussak,  $0·5734 : 1 : 0·9649$ . The thin, elongated prisms have their vertical faces strongly striated, and the crystals are rarely tabular, parallel to (010). Twinning about the twinning plane (110) are common, and there are also contact and penetration twins probably about the plane (112). H. Schneiderhöhn discussed the microstructure. F. Rinne showed that the crystals are isomorphous with those of chalcocite; there is a marked resemblance between the crystals of chalmersite and pyrrhotite. E. Thomson, G. Kalb and M. Bendig, and H. E. Merwin and co-workers emphasized the identity of chalmersite and cubanite. The sp. gr. of chalmersite is 4·04 to 4·68; its hardness 3·5; and its m.p.  $910^\circ$  to  $920^\circ$ . H. E. Merwin and co-workers add that chalmersite is unique in having only one axis, the  $a$ -axis, of high magnetic susceptibility; the susceptibilities of the  $b$ - and  $c$ -axes are feeble. E. Hussak, E. T. Allen, and H. Schneiderhöhn discussed the paragenesis of the mineral.

C. W. Blomstrand<sup>13</sup> described a massive mineral resembling pyrite with a tinge of brown, occurring at Nya Kopparberg, Sweden; he called it **chalcopyrrhotite**, or rather *chalcopyrrhotin*. The analysis corresponds with  $\text{CuFe}_4\text{S}_6$ ; C. W. Blomstrand gave **cupric ferrous ferric hexasulphide**,  $\text{CuS} \cdot \text{Fe}_2\text{S}_3 \cdot 2\text{FeS}$ ; C. F. Rammelsberg,  $\text{Cu}_2\text{S} \cdot 2\text{FeS} \cdot 4\text{Fe}_2\text{S}_3$ ; and P. Groth and K. Mieleitner,  $(\text{Fe}, \text{Cu})_3(\text{FeS}_3)_2$ . The sp. gr. is 4·28, and the hardness 3·5 to 4·0. The mineral **vallerite** from Kaveltorp, described by P. Ramdohr and O. Oedman, has the composition  $\text{Cu}_2\text{Fe}_4\text{S}_7$ .

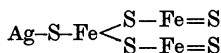
R. Schneider<sup>14</sup> prepared **potassium cuprous ferric tetrasulphide**,  $2\text{K}_2\text{S} \cdot 3\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$ , or  $\text{K}_2\text{Cu}_3\text{FeS}_4$ , by melting together powdered copper and iron with potassium carbonate and sulphur; likewise also with the corresponding **sodium cuprous ferric tetrasulphide**,  $2\text{Na}_2\text{S} \cdot 3\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$ , or  $\text{Na}_2\text{Cu}_3\text{FeS}_4$ . The salts form bronze-coloured rhombic plates, which, according to L. Cambi and L. Szegö, are really

solid soln. with a tetragonal lattice  $a : c = 1 : 1.182$ . R. Schneider found that by treating potassium ferric sulphide with silver nitrate, **silver ferric disulphide**,  $\text{Ag}_2\text{S} \cdot \text{Fe}_2\text{S}_3$ , or  $\text{AgFeS}_2$ , is formed, and with sodium ferric sulphide, **silver ferric tetrasulphide**,  $2\text{Ag}_2\text{S} \cdot \text{FeS}_2$ , or  $\text{Ag}_4\text{FeS}_4$ , is formed—*vide supra*, the sodium salt.

W. Haidinger<sup>15</sup> observed at Joachimsthal, Bohemia, a mineral which he called **sternbergite**—after C. Sternberg. A. Breithaupt called it **silver pyrites**, and C. W. Blomstrand, **argyropyrrhotite**. Analyses, not very concordant, reported by F. H. M. Zippe, C. F. Rammelsberg, and C. Vrba, correspond, in the idealized case, with **silver ferrous trisulphide**,  $\text{AgFe}_2\text{S}_3$ , or  $\text{Ag}_2\text{S} \cdot \text{Fe}_4\text{S}_5$ . W. S. von Waltershausen described another mineral from Joachimsthal, Bohemia, and he called it **argentopyrite**. The analysis corresponded with **silver ferrous pentasulphide**,  $\text{AgFe}_3\text{S}_5$ . G. Cesaro studied these compounds. A. Weisbach also found in the Erzgebirge a mineral which he called **argyropyrite**. The analysis corresponded with **silver ferrous henasulphide**,  $\text{Ag}_3\text{Fe}_7\text{S}_{11}$ . C. Vrba likewise reported a mineral which he called **frieseite**—after M. von Friese. The analyses corresponded with **silver ferrous octosulphide**,  $\text{Ag}_2\text{Fe}_5\text{S}_8$ . They all belong to the rhombic system, and C. Hintze represented their composition and axial ratios as follows :

	$a$	$b$	$c$
Sternbergite, $\text{AgFe}_2\text{S}_3$ . . . . .	0.5832	1	0.8391
Argyropyrrhotite, $\text{Ag}_3\text{Fe}_7\text{S}_{11}$ . . . . .	0.5800	1	0.3000
Frieseite, $\text{Ag}_2\text{Fe}_5\text{S}_8$ . . . . .	0.5970	1	0.7352
Argentopyrite, $\text{AgFe}_3\text{S}_5$ . . . . .	0.5812	1	0.2749

A. Weisbach represented sternbergite by  $\text{Ag}_3\text{Fe}_6\text{S}_9$ , argyropyrite by  $\text{Ag}_3\text{Fe}_7\text{S}_{11}$ , and argentopyrite,  $\text{Ag}_3\text{Fe}_9\text{S}_{15}$ ; and all three minerals by the general formula  $\text{Ag}_3\text{Fe}_{n+6}\text{S}_{2n+9}$ , which he compared with the felspar formula  $\text{Na}_n\text{Ca}_{1-n}\text{Al}_{2-n}\text{Si}_{2+n}\text{O}_8$ , but G. Cesaro does not think there is anything in the comparison. A. Streng compared the formula calculated from the analyses of all the silver pyrites, and concluded that they can be represented as combinations of silver sulphide, *i.e.* **acanthite**,  $\text{Ag}_2\text{S}$ , with  $p\text{Fe}_m\text{S}_n$ , that is, solid soln. of acanthite with pyrrhotite, whilst sternbergite corresponds with the simple formula  $\text{AgFe}_2\text{S}_3$ . C. F. Rammelsberg represented the silver pyrites as mixtures of  $3\text{Ag}_2\text{S} \cdot \text{Fe}_2\text{S}_3$  with  $3\text{FeS} \cdot \text{Fe}_2\text{S}_3$ . G. Cesaro regarded the silver pyrites series as silver sulphoferrites of acids of the general formula  $(n+2)\text{Fe}_2\text{S}_3 \cdot (2m-n-4)\text{H}_2\text{S}$ , where the basicity is  $p = (2m-n-4)/(n+2)$ . For the poly-salt, argentopyrite,  $p = \frac{1}{3}$ , and it is symbolized  $\text{Ag}_2\text{S} \cdot 3\text{Fe}_2\text{S}_3$ ; for the meta-salt, frieseite,  $p = 1$ , and it is symbolized  $\text{Ag}_2\text{S} \cdot \text{FeS} \cdot 2\text{Fe}_2\text{S}_3$ ; for argyropyrite,  $p = 1.4$ , and it lies between the meta- and pyro-salt—the parent acid is supposed to be  $\text{H}_7\text{Fe}_5\text{S}_{12}$ ; and sternbergite is the normal ortho-salt,  $\text{Ag}_2\text{S} \cdot 2\text{FeS} \cdot \text{Fe}_2\text{S}_3$ . He represented argentopyrite by the formula :



and to explain the excess of sulphur in some cases he assumed the existence of complex chains  $-\text{S}-\text{S}-\text{S}=(\text{S}_2)_n$ . Of course, constitutional formulæ have no particular meaning in cases like these, where the composition ranges between limits some distance apart. G. Cesaro later gave for silver pyrites,  $\text{AgFe}_2\text{S}_3$ ; argyropyrrhotite,  $\text{Ag}_3\text{Fe}_7\text{S}_{11}$ ; argentopyrite,  $(\text{Ag}_{10}\text{Fe})(\text{Fe}_7\text{S}_{11})_4$ ; sternbergite,  $\text{Ag}_4\text{Fe}_6\text{S}_{15}$  to  $\text{Ag}_8\text{Fe}_{16}\text{S}_{23}$ ; and frieseite,  $\text{Ag}_6\text{Fe}_{15}\text{S}_{23}$  to  $\text{Ag}_8\text{Fe}_{21}\text{S}_{33}$ . O. Luedecke suggested that the silver pyrites are *morphotrope Mischungen* of sternbergite and marcasite; whilst F. Zambonini regarded the **silver pyrites** as solid soln. of the rhombic sulpho-salt  $\text{AgFe}_2\text{S}_3$ , with rhombic  $\alpha$ -pyrrhotite, when the latter has more or less sulphur in solid soln. This seems one of the most plausible guesses as to the nature of sternbergite and pyrrhotite, and the hypothesis was supported by V. Nikitin.

Sternbergite occurs in implanted crystals forming rose-like or fan-like aggregates which are coloured pinchbeck-brown with a violet tarnish on some of the faces. The axial ratios of the rhombic crystals were found by W. Haidinger to be 0.5832 : 1 : 0.8391. Twinning occurs about the (110)-plane; and the crystals may

be tabular, parallel to (001). The (001)-faces may be striated parallel to the (001)/(301)-edge. The pyramids are striated parallel to the intersection with the (001)-face. The (001)-cleavage is perfect, and the thin laminae are flexible like tin-foil. The crystals were discussed by W. H. Miller, V. Goldschmidt, and J. D. Dana. W. Haidinger gave 4·215 for the sp. gr., and A. Breithaupt, 4·101; the hardness is 1·0 to 1·5, and the mineral, like graphite, leaves a trace on paper. F. Beijerinck found that the mineral is a good electrical conductor. C. Doelter synthesized sternbergite by warming a mixture of ferric oxide and silver chloride in a current of hydrogen chloride. The artificial crystals were cubic octahedra, so that the compound may be dimorphous.

Argyropyrite occurs in bronze-yellow crystals which, according to A. Weisbach, are rhombic with the axial ratios  $a : b : c = 0·5731 : 1 : 0·2968$ , or  $0·5859 : 1 : 0·30176$ . The sp. gr. is 4·1 to 4·2, and the hardness, 3 to 4. Argentopyrite was said by W. S. von Waltershausen to occur in steel-grey or tin-white, monoclinic, six-sided twin crystals with no cleavage; and G. Tschermak observed pseudomorphs in small hexagonal crystals; but A. Schrauf showed that the crystals of argentopyrite are really rhombic and are pseudohexagonal by repeated twinning. The axial ratios are  $a : b : c = 0·5812 : 1 : 0·2749$ , like sternbergite if the  $c$ -axis be multiplied by 3. The sp. gr. is 5·5 or more, and the hardness, 3 to 4. F. Beijerinck said that the mineral is a good electrical conductor. Frieseite occurs in thin, translucent, dark greenish-grey plates belonging to the rhombic system, and, according to C. Vrba, having the axial ratios  $a : b : c = 0·5970 : 1 : 0·7352$ . Twinning occurs about the (110)-plane. The tabular crystals are parallel to (001), and the (001)-faces are striated parallel to the (001)/(111)-edge. There may be feather-like striations on the twins. The (001)-cleavage is perfect, and the laminae are flexible. The sp. gr. is 4·212 to 4·220, and the hardness 1 to 2.

H. Malfatti<sup>16</sup> prepared **calcium ferric sulphide**,  $\text{Ca}(\text{FeS}_2)_2$ , by treating mixtures of hydrated ferric oxide, and calcium hydroxide with hydrogen sulphide, and **barium ferric sulphide**,  $\text{Ba}(\text{FeS}_2)_2$ , in a similar way. J. Thugutt treated a mixture of hydrated ferric oxide and magnesium hydroxide with hydrogen sulphide, and obtained **magnesium ferric hydroxysulphide**,  $(\text{Mg}(\text{OH})_2 \cdot \text{Fe}_2\text{S}_3 \cdot 2\text{H}_2\text{O})$ . R. Schneider prepared **cadmium ferric disulphide**,  $\text{CdS} \cdot \text{Fe}_2\text{S}_3$ , and **cadmium ferrous sulphide**,  $2\text{CdS} \cdot \text{FeS}$ , by the methods employed for the silver salts.

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## § 42. The Iron Sulphides—Iron Disulphide.

La pyrite est à l'industrie chimique ce que le pain est à l'alimentation de l'homme.—  
P. TRUCHOT.

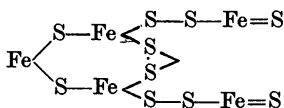
The term **pyrites**— $\pi\upsilon\rho$ , fire—was employed by the ancients to denote a number of minerals which gave sparks when struck with a hammer. It was employed by Dioscorides, in his *De materia medica* (5. 89), and by Pliny, in his *Historia naturalis* (36. 30), at the beginning of our era, for copper and iron pyrites, as well as for *molares* or mill-stones. Pliny's use of the term is analogous to the use of  $\sigma\pi\upsilon\sigma$  by Theophrastus, in his *Περί λίθος* (19), written about 315 B.C. According to E. O. von Lippmann,<sup>1</sup> the *misy* of Dioscorides and Pliny, was probably a form of copper pyrites. According to G. Hoffmann, the Grecian word  $\piυ\rho\rho\eta\varsigma$  is synonymous with the *marquashūha* of the Arabians, a term borrowed from the Aramæans, and employed by Aby Mansur Muwaffak, an Arabian writer of the tenth century. The term appeared later as *marcasite* for a variety of pyrite. Geber, in his *Summa perfectionis magisterii*, and other writings, employed the term *marcasite* for pyrites, and, still later, as pointed out by E. Darmstädter, it was applied by the pharmacutists of the Middle Ages to bismuth (*q.v.*). G. Agricola translated the term pyrites by *Kis*, and J. F. Henckel designated crystalline pyrites *marchasita*. G. Agricola appears to have regarded copper pyrites as a variety of iron pyrites. J. G. Wallerius classed different varieties of *sulphur ferro mineralisatum* as (i) *Kies*, or iron pyrites; (ii) *Marcasite*; (iii) *Wasserkies*. Analogous classifications were made by L. A. Emmerling, and A. Breithaupt. J. Hill called the globular form *pyrites*, the crystalline form *marcasite*, and the massive form *mundic*. The term

marcasite was used by the old writers for antimony and bismuth. The *white pyrites*, *Wasserkies*, or *pyrites fuscus lamellosus* of J. G. Wallerius, received various terms in allusion to its paler colour, and in allusion to cockscomb or spear-shaped crystals. J. B. L. Romé de l'Isle, and R. J. Haüy at first regarded it as an irregular variety of common pyrites, but later, he distinguished between the prismatic, rhombic, or white pyrites, and the ordinary form crystallizing in various modifications of the cube. The analyses of J. J. Berzelius, and C. Hatchett established the chemical identity of the two varieties, for both had a composition approaching  $\text{FeS}_2$ , and accordingly R. J. Haüy spoke of the *la dimorphie de fer sulfuré*. W. Haidinger applied the term **marcasite** to the white or prismatic variety, and **pyrite** to the cubic form. Both varieties can be included in the general term pyrites—A. Breithaupt used the term marcasite in this general way.

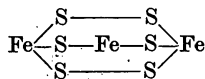
The terms *Wasserkies* and *Lebererz* were applied by G. Agricola, A. Cronstedt, and J. F. L. Hausmann to the marcasite variety. A. Cronstedt translated it *pyrites aquosus*, which, as J. D. Dana said, has little applicability, but may have been used in allusion to the greater tendency of the mineral to become moist and to weather than is the case with pyrite. G. Agricola considers the term *Wasserkies* to be an early corruption of *Weisserkies*—white iron pyrites. The term was also used for easily decomposable pyrites and hence pyrrhotite was included. A. Breithaupt translated G. Agricola's *Lebererz* as *hepatopyrites*, and E. F. Glocker translated the *Wasserkies* as *hydropyrites*. The white copper ore of J. F. Henckel was called by A. G. Werner, L. A. Emmerling, and A. Breithaupt, *Weisskupfererz*, and the light colour was attributed to the presence of arsenic. It was thought by A. Breithaupt to have *chemisch gebundenes Wasser*, and to be a definite mineral species—which he called *hydropyrites*—but J. J. Berzelius, and J. F. L. Hausmann did not regard it as a mineralogical individual. A. Breithaupt used the term *lonchidite*—a diminutive form:  $\lambda\omicron\gamma\chi\iota\delta\iota\omicron\nu$  of  $\lambda\omicron\gamma\chi\eta$ , the head of a javelin—for a variety of marcasite, with about 5 per cent. of arsenic; also *kyrosite*—from  $\kappa\upsilon\rho\omega\sigma\iota\varsigma$ , a confirmation—for another arsenical variety which J. J. Berzelius considered to be more probably a mixture of copper sulphide and arsenical pyrites; and F. Sandberger called another variety of marcasite with about 2.7 per cent. of arsenic, *metalonchidite*. A variety of pyrite from Ribadeo, Galicia, containing tin and zinc, was called by G. Schulz and A. Paillette, *ballesterosite*—after L. Ballesteros. S. L. Penfield showed that the *blueite*, and *whatonite* of S. H. Emmons, are nickeliferous varieties of pyrite.

Numerous analyses and descriptions of pyrite have been reported—e.g., by C. F. Rammelsberg,<sup>2</sup> M. Amelung, C. von Hauer, G. A. Kenngott, J. F. Williams, C. Mène, A. d'Achiardi, F. A. Genth, E. C. Schiffer, V. Pöschl, E. G. de Angelis d'Ossat, A. Piutti and E. Stoppani, C. von John and C. F. Eichleiter, E. H. Kraus and J. D. Scott, J. Samojloff, E. T. Allen and co-workers, A. Liffa, E. Arbeiter, K. Bornemann and O. Hengstenberg, F. Kolbeck, H. Laspeyres, S. L. Penfield, W. Vernadsky, T. L. Walker, H. H. Knox, J. H. L. Vogt, C. Doelter, E. Weinschenk, A. Girard and H. Morin, G. Lunge, A. Voelcker, A. Eschka, M. Watanabe and W. R. Landwehr, G. H. Thiel, etc. The results are well summarized by the formula  $\text{FeS}_2$ . Samples containing some nickel,  $(\text{Fe}, \text{Ni}, \text{Co})\text{S}_2$ , were reported by W. H. Emmons, S. L. Penfield, F. Kolbeck, and H. Laspeyres; cobalt, by H. Laspeyres, F. Kolbeck, W. Vernadsky, and E. Ebermayer. The presence of gold, and silver in pyrite was discussed by A. Schmidt, F. Behrend, E. Nowak, H. Bücking, J. Samojloff, A. Kromayer, W. Mietzschke, and G. H. F. Ulrich. W. N. Hartley and H. Ramage found sodium, potassium, copper, silver, and calcium in all the samples they examined, and gallium, indium, thallium, lead, manganese, and nickel in some of them. L. Lukacs found calcium, gold, mercury, arsenic and antimony in a number of samples. H. N. Stokes, and many others have discussed cupriferous pyrites; L. C. Marquart reported up to 5 per cent. of thallium in some pyrites—*vide* 5.36, 1. C. U. Shepard applied the term *teluspyrine* to a telluriferous pyrite from Sunshine Camp, Colorado; W. N. Hartley and H. Ramage, and others have noted the presence of selenium in pyrites. G. Schulz and A. Paillette found zinc and tin in some pyrites. Arsenical pyrite, and manganiferous pyrite were discussed by W. Vernadsky. W. N. Hartley and H. Ramage found platinum in some varieties.

Many investigators have assumed that pyrite contains both ferrous and ferric iron, and that the molecule is accordingly complex. N. S. Kurnakoff and co-workers assumed that the marked contraction which occurs in the formation of pyrite from its elements, as well as the great hardness of pyrite agree with the assumption that the molecule is highly polymerized  $(\text{FeS}_2)_n$ . P. Groth suggested that the molecule is doubled,  $n=2$ , and added that the iron is probably present in the ferrous state. E. Weinschenk, for instance, regarded this sulphide as a kind of magnetite and represented it by the formula  $(\text{FeS}_2)_3$ , in which one-third of the iron is ferrous, and two-thirds, ferric. This is supposed to be supported by C. F. Rammelsberg's observations:



W. B. Brown's formula



E. Weinschenk's formula

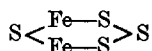
on the formation of pyrite by heating magnetite in an atm. of hydrogen sulphide. A. P. Brown's experiments indicated that while in marcasite all the iron is in the ferrous state, in pyrite, one-fifth is in the ferrous state, and four-fifths in the ferric state. He therefore gave  $4\text{Fe}'''\text{S}_2$  (*vide supra*) for the formula of pyrite, and  $\text{Fe}''\text{S}_2$  for marcasite. H. N. Stokes could find no difference in the relative proportions of ferrous and ferric iron in marcasite and pyrite—*vide infra*, pyrite. E. Weinschenk said that the formula,  $\text{S}=\text{Fe}-\text{S}-\text{S}-\text{Fe}=\text{S}$ , which assumes all the iron in pyrite to be ferric, is not probable because of the easy reducibility of the ferric sulphide; H. N. Stokes based a similar conclusion on the fact that ferric oxide is formed by the action of zinc carbonate in an alkaline soln., and in the absence of an oxidizing agent, on pyrite and marcasite, and he suggested that these minerals should be formulated  $\text{Fe}_2\text{S}_3(\text{S})$ . It will be remembered that in deducing conclusions from reactions of this type, it is assumed that during the reaction there is no essential change in the arrangement of the atoms of the iron compound when the sulphur atoms are displaced by oxygen. The different conclusions obtained by studying different reactions show that what elsewhere has been called the rule of the constancy of structural arrangement cannot be depended upon. J. Loczka showed a formula,



J. Loczka's formula

which assumes the iron to be all in the ferrous state, and is in agreement with the fact that on weathering, pyrite furnishes ferrous sulphate and sulphuric acid. This is in accord with the observations of P. Groth, C. Doelter, L. Benedek, E. T. Allen and co-workers, and G. W. Plummer; and with the X-radiograms observed by W. L. Bragg, A. Reis, M. L. Huggins, J. Beckenkamp, P. P. Ewald and W. Friedrich, and P. Niggli—*vide infra*, pyrites. L. C. Jackson also found that the magnetic properties of pyrite indicate that iron is present in the ferrous form. Pyrite may belong to a persulpho-salt analogous to the peroxy-salts typified by barium dioxide,  $\text{BaO}_2$ . The constitution of pyrite with bivalent iron is then represented either by  $\text{Fe}=\text{S}=\text{S}$  or by J. Loczka's formula (*vide supra*). The twinning of the sulphur atoms favours the assumption that iron pyrites is a ferrous disulphide,  $\text{Fe}^{++}-\text{S}-\text{S}-$ , containing a bivalent diatomic anion, as in the case of such peroxides as  $\text{Na}^+\text{O}^--\text{O}^--\text{Na}^+$ ; and of the mercurous ion  $\text{Hg}^+-\text{Hg}^+$  in mercurous nitrate. The assumption is made by A. Werner that the iron is quadrivalent in pyrite,  $\text{S}=\text{Fe}=\text{S}$ ; and this hypothesis is modified by P. Pfeiffer who assumed that pyrite has the complex radicles  $[\text{Fe}(\text{S}_2)_6]$  and  $[(\text{S}_2)\text{Fe}_6]$ . E. Arbeiter studied the oxidation of pyrite by hydrogen dioxide, and concluded that one-fourth of the sulphur is differently oriented from the remaining three-fourths because it is more readily

oxidized. Consequently, in agreement with A. Beutell's formula for cobaltite, E. Arbeiter represented the constitution of pyrite :



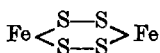
E. Arbeiter's formula

Analyses of marcasite, made at the beginning of the nineteenth century, by C. Hatchett,<sup>3</sup> and J. J. Berzelius showed that its ultimate composition is the same as that of pyrite, namely,  $\text{FeS}_2$ . This was confirmed by the work of F. J. Malaguti and J. Durocher, A. Vogel and C. Reischauer, F. Sandberger, C. Trapp, C. F. Plattner, C. H. Scheidhauer, J. A. Antipoff, E. Arbeiter, E. T. Allen and co-workers, E. Ammermann, E. Manasse, F. Schöndorf and R. Schröder, G. Sirovich, A. Breithaupt, etc. M. J. Buerger concluded that the published analyses show that pure pyrite has the composition  $\text{FeS}_2$ , and marcasite  $\text{FeS}_{1.985}$ . The proportion of arsenic was discussed by E. Arbeiter, and B. Kosmann—*vide* arsenopyrite, and löllingite; the nickel and cobalt, by B. Kosmann; and the thallium, by A. Breithaupt.

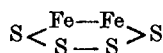
C. F. Rammelsberg regarded arsenical marcasite as a mixture of, say,  $26\text{FeS}_2$  and  $\text{FeAs}_2$ ; and A. Beutell discussed this subject regarding  $\text{FeS}_2$  and  $\text{FeAs}_2$  as isomorphous, a subject discussed by J. W. Retgers, and A. Arzruni. W. B. Brown supposed that marcasite contained only ferrous iron, and should be represented :



W. P. Brown's formula



A. Beutell's formula



E. Arbeiter's formula

A. Beutell used the doubled formula just indicated, and it was favoured by P. Groth. E. Arbeiter showed that when oxidized with hydrogen dioxide, half the sulphur atoms behave differently from the other half in agreement with the assumption that they are differently oriented in the molecule as just indicated. F. Beijerinck favoured the ring formula; and M. L. Huggins gave a possible structure for the space-lattice—*vide infra*.

The history and composition of dimorphic **pyrites**, that is, **iron disulphide**,  $\text{FeS}_2$ , as it appears in the form of cubic **pyrite** and rhombic **marcasite**, has been previously discussed in connection with the iron sulphides. G. Königsberger and O. Reichenheim<sup>4</sup> believed that a third modification appears at  $400^\circ$ , but E. T. Allen and co-workers, and E. Arbeiter were unable to confirm the existence of forms of the disulphide other than marcasite and pyrite. As indicated below, there is a colloidal form of the disulphide. Pyrite occurs sparingly though frequently in rocks of all ages—from the oldest igneous rocks, to the later metamorphic rocks, and comparatively recent alluvial deposits; it was called by J. F. Henckel, in 1725, the *Jack-in-every-street-Pyrite*. It is commonly associated with magnetite or hæmatite, and in the neighbourhood of metallic veins, it may be accompanied by metal sulphide—*e.g.*, chalcopyrite, bornite, chalcocite, sphalerite, galena, etc. According to A. A. Julien, pyrite tends to predominate in the crystalline rocks largely constituted of magnesia- and iron-micas, hornblende, chlorite, and serpentine such as diorite, chlorite- and hornblende-schists, etc. It is prominent as well in weathered eruptive rocks and most granites, marbles, and clays; it occurs scattered in anthracite and nearly all metalliferous veins, and in clay beds. The pyritic deposits in nature have a widely different origin and history. (i) Some have crystallized directly from rock magmas, and were formed at a high temp., thus, J. H. L. Vogt found that the iron sulphides are soluble in silicate magmas at high temp., and that they are amongst the earliest minerals to crystallize from such magmas. (ii) Others are formed by contact metamorphism, and they may be connected with the eruption of igneous rocks although high temp. minerals are usually absent, and the gangue contains barite and calcite, as well as quartz—*e.g.*, the deposits of

Rio Tinto, Spain, discussed by J. H. Collins, A. M. Finlayson, F. Klockmann, L. de Launay, H. Preiswerk, J. Gonzalo y Tarin, J. H. L. Vogt, B. Wetzig, etc.; the deposits of Rammelsberg, Harz, Germany, discussed by F. Klockmann,<sup>5</sup> J. H. L. Vogt, W. Lindgren and J. D. Irving, etc.; and the deposits of Mount Lyell, Tasmania, discussed by J. W. Gregory. (iii) Another class is generally thought to represent a phase of igneous injection for they have a close relation to the igneous rock formations—e.g., the Norwegian deposits at Vignas, Sulitelma, and Røros; the Swedish deposits at Fahlun and Bersbo; and the Bavarian deposit at Bodenmais. All these deposits may have been modified in structure and mineral association by dynamic metamorphism. W. A. Tarr noted sulphide inclusions in Joplin calcites, and also alternating deposits of pyrite and marcasite. Marcasite, said he, is deposited by acidic soln., pyrite by neutral or slightly acidic soln., and melnikovite by alkaline soln. The occurrence of pyrites is discussed by P. Truchot, *Les pyrites* (Paris, 1907), and by A. W. G. Wilson, *Pyrites in Canada* (Ottawa, 1912); and the paragenesis, by W. H. Newhouse.

Pyrite and other sulphides may be precipitated by chemical reactions in sediments, and thus appear in sedimentary formations—clays, shales, marls, limestone, coal, etc. In many cases, the pyrites is supposed to have been formed by the reduction of soln. of iron sulphate by organic matter. M. Longchamp<sup>6</sup> observed iron pyrites as a deposit from the mineral water in a narrow channel of the thermal spring at Chaudesaigues; J. J. Noggerath found the limestone in the thermal springs of Aix-la-Chapelle was covered with a film of pyrites; and G. Bischof made analogous observations. He also found that water containing sulphates and organic matter was able to convert ferrous carbonate into pyritic crystals. A. Liveridge mentioned a case of the formation of pyrite on twigs in the hot spring at Tempo, New Zealand; and H. Kiefer, in the rocks of the Upper Rhine; J. L. G. Meinecke found the wood in a swamp at Dölau was incrustated with pyrites; L. W. Gilbert, and H. F. Link made similar observations. R. Bakewell showed that some mouse droppings accidentally kept in a flask in contact with a soln. of ferrous sulphate for some time, became covered with crystals of pyrites. Observations on the subject were made by G. Forchhammer, A. Daubrée, C. W. C. Fuchs, F. Fouqué and A. Michel-Lévy, and F. J. Malaguti and J. Durocher. A. Gautier discussed the formation of hydrogen sulphide by the decay of organic matter. According to M. W. Beyerinck, certain micro-organisms—bacteria, algæ, infusoria, and flagellata—favour the formation of pyrites in surface soils by evolving hydrogen sulphide as a product of the reduction of sulphates. J. von Fodor said that micro-organisms in soils have been discovered only at a depth of about 5 metres. Observations on the formation of pyrites by the reduction of sulphates by swamp water, spring water, etc., were made by A. R. Whitman, C. O. Harvey, V. Rodt, C. Ochsenius, W. Feld, H. Schneiderhöhn, R. Brauns, A. Lacroix, H. Winter and G. Free, and E. Joukowsky. G. Sirovich did not favour the hypothesis that pyrites is formed, geologically, by the reduction of ferrous sulphate soln. by organic matter:  $7C + 4FeSO_4 = 2FeCO_3 + 2FeS_2 + 5CO_2$ ; nor did E. T. Allen and co-workers obtain satisfactory results in the reduction of ferrous sulphate soln. by starch and glucose, even at temp. as high as 300°; but the frequent occurrence of pyrites on coal, and its occasional formation on wood, indicate that the reduction may occur.

According to E. T. Allen and co-workers, the sulphide produced by ascending waters is always pyrite, never marcasite, and such waters are naturally hot, and nearly always alkaline. A. Daubrée noted the formation of pyrite in the springs of Carlsbad where the temp. is about 55°. The deposition of pyrites by the Tuscan lagoons, was observed by J. Nöggerath and G. Bischof; R. Bunsen noted that the hot vapours of the fumaroles in Iceland are slowly converting the ferrous silicate of the rocks into pyrites; and A. Lacroix observed that pyrite and pyrrhotite were formed in the eruption of Vesuvius in April, 1906, owing to the action of hydrogen sulphide on the volatilized ferrous chloride. E. T. Allen and co-workers found that

both marcasite and pyrite can be formed by the agency of hydrogen sulphide under geological conditions ; and added that pyrite, in the majority of cases, and marcasite, in all cases, crystallize from aq. soln. The pyrite of deep veins, metamorphic contacts, thermal springs, and magmas has been formed by *hot* soln., and these soln. never contain strong mineral acids, but are generally, if not always, alkaline. The pyrite and marcasite of surface veins, on the other hand, are formed from *cold* soln. which often contain a relatively high proportion of sulphuric acid.

J. R. Blum<sup>7</sup> described pseudomorphs of pyrite after barytes ; A. Breithaupt, after fluorite ; G. vom Rath, after magnesite ; K. Zimanyi, after calcite ; G. Tschermak, after augite ; E. Döll, after tourmaline, and epidote ; and F. Schumacher, after biotite. Fossils also may consist of pyrites when the mineral has been formed by the reduction of soln. of ferrous sulphate by organic matter ; and it may also explain the formation of nodules of pyrite and marcasite found in clays, and chalk beds. A. Gautier, for instance, showed that hydrogen sulphide is one of the products of the putrefaction of organic matter, and that the pyrite which forms the substance of some fossil bones and shells is precipitated by hydrogen sulphide given off by the decomposing organic matter. This subject was discussed by P. Fallot, and E. Joukowsky.

Unlike pyrite, marcasite does not occur as a primary constituent of magmas, because, as shown by E. T. Allen and co-workers,<sup>8</sup> marcasite is unstable at temp. exceeding 450°—*vide infra*. Marcasite occurs only in sedimentary deposits, and metalliferous veins. It is formed in surface veins from cold acidic soln., and mixtures of pyrite and marcasite may have been formed at higher temp., up to, say, 300°, or in the presence of less acid, or both. The formation of pyrite is favoured by alkaline soln., and temp. exceeding 450°. G. V. Douglas, F. R. and K. R. Horn, V. R. von Zepharovich, T. Brandes, T. Scheerer, H. N. Stokes, W. S. T. Smith and C. E. Siebenthal, and E. T. Allen and co-workers observed marcasite and pyrite associated together in concentric layers, etc. C. Hintze mentions thirty-one cases where the two minerals have intergrown or been precipitated one on the other. As in the case of pyrite (*q.v.*), it may be formed by what appears to be the reduction of sulphate soln., as observed by E. F. Glocker. A. A. Julien said that marcasite is largely or wholly the pyrites of thin seams and coatings in coal-beds, lignitic shales, dolomites, limestones, and in general unaltered sedimentary rocks like sandstones, graywacke schists, peat, clay, bituminous coals, casts of fossils, and veins of galena. It occurs in stalactitic forms. E. Kalkowsky observed incrustations—*marcasite patina*—on some wooden piles. Spear-shaped crystals occur in the plastic clay of the brown coal formation of Littmitz, and Altsattell, Bohemia, where it was mined for its sulphur, and the manufacture of ferrous sulphate. C. Winkler described cryptocrystalline pyrites formed in the inside of cast-iron tubes conveying sulphide liquors in the manufacture of sodium carbonate ; these crystals, according to C. Doelter, are marcasite. C. Reidemeister observed the crystals were formed in the joints of a plant used for the purification of sulphur. Pseudomorphs of marcasite after many minerals have been observed. H. Schneiderhöhn noted the following sequence : siderite→pyrrhotite→marcasite→pyrite ; and E. Döll also noted pseudomorphs of pyrite after marcasite. J. F. L. Hausmann reported small crystals of pyrite in the sole of an old roasting furnace in the Harz. B. von Cotta also observed pyrites as a furnace product ; and G. Lowe observed that in the sublimation, at a dull red-heat, of ammonium chloride containing some sulphate from an iron vessel lined with clay, cubes and octahedra of pyrites were formed on the surface of the clay.

The separation of pyrites from other minerals by electrostatic and electromagnetic processes was discussed by P. André,<sup>9</sup> T. Crook, G. Rigg, P. Truchot, P. Rehbinder and co-workers, and A. W. G. Wilson.

**The preparation of iron disulphide—pyrite and marcasite.**—J. L. Proust, C. F. Bucholz and A. F. Gehlen, J. J. Berzelius, C. F. Rammelsberg, L. Gedel, and R. Scheuer obtained iron disulphide by heating a mixture of iron or ferrous

sulphide and sulphur below a red-heat. According to J. J. Berzelius, when ferric oxide or its hydrate, ferrosic oxide, ferrous carbonate, or one of the lower iron sulphides is exposed to the action of hydrogen sulphide at a temp. short of redness, a vigorous reaction at first occurs, and steam, sulphur dioxide, and hydrogen are evolved whilst a lower sulphide of iron is formed, which afterwards takes up more sulphur with the evolution of hydrogen. J. J. Berzelius also said that when an intimate mixture of ferrous sulphide with half its weight of sulphur is heated in a retort to a temp. short of redness, iron disulphide is formed as a bulky, yellow powder. J. J. Berzelius, C. Doelter, L. Gedel, T. G. Pearson and P. L. Robinson, and L. A. Sayce added that hydrogen sulphide at a low temp., between  $100^{\circ}$  and a red-heat, forms iron disulphide, but C. F. Rammelsberg added that the product is an oxysulphide, not the disulphide. F. Wöhler heated an intimate mixture of ferric oxide, sulphur, and ammonium chloride to a temp. a little above the sublimation point of the ammonium chloride, and obtained a residue consisting of small, brass-yellow octahedra and cubes of pyrite which could be separated from the rest of the powder by levigation. S. Meunier added that various salts of iron—*e.g.*, ferrous carbonate—can be employed in place of ferric oxide. F. Foreman, and E. Weinschenk obtained crystals by a similar process. C. F. Rammelsberg melted iron with an excess of sulphur, and obtained a mass similar to pyrites, and by the action of hydrogen sulphide on siderite or magnetite, between  $100^{\circ}$  and  $500^{\circ}$ , he obtained pseudomorphs of pyrite. J. Durocher passed a mixture of the vapour of ferric chloride and hydrogen sulphide through a red-hot porcelain tube, and obtained small cubic crystals; whilst F. Schlagdenhauffen also obtained the crystals by the action of the vapour of carbon disulphide on ferric oxide at a high temp. E. Glatzel heated in a retort an intimate mixture of phosphorus pentasulphide with twice its weight of anhydrous ferric chloride, until thiophosphoryl chloride was no longer evolved, and after levigation in water, isolated crystals of pyrite remained. According to N. Costeanu, sodium or potassium pentasulphide can be employed in place of phosphorus pentasulphide. H. N. Warren obtained pyrite by heating a mixture of ferric oxide and potassium thiocyanate. C. Doelter showed that in the experiments of J. Durocher, and C. F. Rammelsberg, the reaction occurs at about  $200^{\circ}$ , and that it is better to use amorphous ferric oxide than hæmatite or metallic iron. C. Geitner obtained brass-yellow crystals of pyrite by heating iron, magnetite, or ferric oxide and sulphurous acid in sealed tubes at  $200^{\circ}$ .

H. de Sénarmont heated a soln. of potassium or sodium polysulphide with ferrous or ferric sulphate in a sealed tube at  $180^{\circ}$ , and obtained a yellow product; and by heating precipitated ferrous sulphide with a soln. of hydrogen sulphide in a sealed tube, he obtained crystals of pyrite; a black precipitate obtained in this process is considered by L. Gedel to be ferric sulphide. E. T. Allen and co-workers represented the reactions:  $\text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{S} = 2\text{FeSO}_4 + \text{H}_2\text{SO}_4 + \text{S}$ , and  $\text{FeSO}_4 + \text{S} + \text{H}_2\text{S} = \text{FeS}_2 + \text{H}_2\text{SO}_4$ . A. Schleede and H. Buggisch employed an analogous process; and C. O. Harvey boiled a soln. of ferrous sulphate with hydrogen sulphide, water, sulphur, and chalk:  $\text{FeSO}_4 + \text{H}_2\text{S} + \text{CaCO}_3 = \text{H}_2\text{O} + \text{CO}_2 + \text{FeS}_2 + \text{CaSO}_4$ . C. Doelter heated in sealed tubes a mixture of siderite, hæmatite, or magnetite with water saturated with hydrogen sulphide for 72 hrs. at  $80^{\circ}$  to  $90^{\circ}$ , and obtained cubic crystals of pyrite. Siderite gave the best results; only a small yield was obtained with magnetite. C. Doelter also heated ferrous chloride, water, and hydrogen sulphide in a sealed tube for 16 days at  $200^{\circ}$ , and he obtained pyrrhotite when air was excluded, and pyrite when some air was present. C. Doelter also noticed that crystals of pyrite were formed in his experiments on the solubility of pyrite in water, and in soln. of sodium sulphide. The black, amorphous precipitate formed by the action of alkali polysulphides on ferrous salts, is, according to E. T. Allen and co-workers, a mixture of ferrous sulphide and sulphur. This mixture, when heated, gradually passes into the disulphide, although some black precipitate remains unchanged even after heating for several days with an excess



of polysulphide at 100°. The influence of time is shown by heating systems with 3 grms. of ferrous sulphate, 2.5 grms. sodium sulphide, 0.75 gm. sulphur, and 100 c.c. of water at 100° for 2 and 7 days, when the products contained respectively 75 and 95 per cent. of pyrite. E. T. Allen and co-workers found that when the products are purified by boiling with 20 per cent. hydrochloric acid, the proportions of pyrite formed at 300°, 200°, and 100° were respectively 97, 71, and 51 per cent. Marcasite was absent, so that the remaining 3, 29, and 49 per cent. are amorphous disulphide. The evidence for the existence of the amorphous disulphide in the alkaline soln. is as follows: While the products of acidic soln. which contain the most marcasite are the best crystallized, those from alkaline soln. which contain the most disulphide are almost black, dull, and lustreless at the lower temp. The proportion of pyrite is increased by raising the temp., or prolonging the time of the reaction—both conditions are favourable to the production of an amorphous substance. Moreover, marcasite is not changed when it is heated several days with a soln. of sodium polysulphide at 300°. Hence, the first product of the union of sulphur and ferrous sulphide from an alkali polysulphide soln. is amorphous iron disulphide which slowly crystallizes into pyrite.

According to E. T. Allen and co-workers, the first action of hydrogen sulphide on a soln. of a ferric salt is to reduce the soln. with the simultaneous deposition of sulphur; and in closed vessels, when the hydrogen sulphide cannot escape or be oxidized, the reaction:  $\text{FeSO}_4 + \text{S} + \text{H}_2\text{S} = \text{FeS}_2 + \text{H}_2\text{SO}_4$ , occurs. The speed of this reaction is very small at ordinary temp., but at 200° it is comparatively rapid. When hydrogen sulphide and sulphur act on a soln. of ferrous sulphate, the crystals of the disulphide are small; their size is greater the higher is the temp.; other conditions—e.g., a slow reaction—favour the formation of large crystals. Thus, by arranging the experiment at 200° so that hydrogen sulphide was slowly given off from a thiosulphate soln.,  $\text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O} = \text{Na}_2\text{SO}_4 + \text{H}_2\text{S}$ , in the presence of a ferric salt, comparatively large crystals of a mixture of pyrite and marcasite were formed. In order that pyrite may be the principal product, the soln. should be neutral, or only slightly acid. The reaction which occurs when a mixture of ferrous sulphate and sodium thiosulphate is heated in a sealed tube at 90° to 200°, results in the formation of a mixture of sulphur and pyrite. The reaction can be symbolized:  $4\text{Na}_2\text{S}_2\text{O}_3 + \text{FeSO}_4 = \text{FeS}_2 + 3\text{S} + 4\text{Na}_2\text{SO}_4$ . It is possible that in the case of ferrous sulphate, the hydrogen sulphide from the thiosulphate reacts:  $\text{FeSO}_4 + 4\text{H}_2\text{S} = \text{FeS}_2 + 3\text{S} + 4\text{H}_2\text{O}$ ; but since the pyrite is similarly formed with soln. of ferrous chloride, it is thought that ferrous thiosulphate is first formed:  $\text{FeSO}_4 + \text{Na}_2\text{S}_2\text{O}_3 = \text{Na}_2\text{SO}_4 + \text{FeS}_2\text{O}_3$ ; and that this reacts:  $\text{FeS}_2\text{O}_3 + 3\text{Na}_2\text{S}_2\text{O}_3 = \text{FeS}_2 + 3\text{S} + 3\text{Na}_2\text{SO}_4$ . Pyrite was also synthesized by the thiosulphate reaction by W. Feld, and R. F. Carpenter and E. Linder. W. Mecklenburg and V. Rodt, and V. Rodt found that in the absence of air, ferric sulphide decomposes into pyrite and ferrous sulphide:  $\text{Fe}_2\text{S}_3 = \text{FeS} + \text{FeS}_2$ .

According to E. T. Allen and co-workers, hydrated ferric oxide along with 100 c.c. of water saturated with hydrogen sulphide, was heated in a sealed tube for 7 days at 140°, and the yellowish-brown product was boiled with 20 per cent. hydrochloric acid to remove hydrated ferric oxide and ferrous sulphide. About 90 per cent. of the remainder was pyrite, and 10 per cent. marcasite. Hydrated ferric oxide which has been dried at 100° is less susceptible to attack by hydrogen sulphide than the hydrate which has not been dried. In these cases, the pyrite is immediately formed by the direct union of sulphur and ferrous sulphide, as shown by C. Doelter, —the hydrogen sulphide water probably acts as a weak solvent; similarly also marcasite can be regarded as a product of the addition of sulphur to ferrous sulphide which gradually forms from the soln. Since pyrite can be formed by the action of sulphur on crystalline pyrrhotite, it follows, as pointed out by E. T. Allen and co-workers, that it is not the exact nature of the solid phase reacts with the sulphur, but rather the composition of the soln. in which it forms, which determines whether the product shall be pyrite or marcasite. A mixture of 2.2 grms. of artificial

pyrrhotite, 0.8 grm. of sulphur, 0.1 grm. of sodium hydrocarbonate, and 100 c.c. of water was saturated with hydrogen sulphide, and sealed in a glass tube. The composition of the soln. was similar to that of a warm "sulphur" spring, and it served as a solvent for the sulphur which was gradually absorbed by the pyrrhotite. The vessel was heated for 2 months at 70°, when the undecomposed pyrrhotite was removed by boiling the product with 20 per cent. hydrochloric acid. The dense, brass-yellow product contained all pyrite and no marcasite. The reaction proceeds more quickly at 300°; thus, a mixture of 5 grms. of pyrrhotite, 1.75 grms. sulphur, 0.2 grm. of sodium hydrocarbonate, and 100 c.c. of water saturated with hydrogen sulphide, was similarly treated for 4 days at 300°, when the product contained 95 per cent. pyrite. V. Rodt prepared pyrite by boiling a mixture of freshly-precipitated ferrous sulphide and sulphur suspended in water; and it is formed by the action of hydrogen sulphide on hydrated ferric oxide when the first product of the action is ferric sulphide, and if at an elevated temp., the ferric sulphide decomposes into iron disulphide. The reaction:  $\text{Fe}_2\text{S}_3 \rightarrow \text{FeS} + \text{FeS}_2$ , does not occur in the presence of substances having an alkaline reaction. A. L. T. Moesveld observed pyrite is formed in faintly-alkaline or neutral soln., and marcasite, in acidic soln. L. A. Sayce found that pyrite is formed when hydrogen sulphide, at about 300°, acts on ferric oxide (*q.v.*).

V. Rodt, and W. Feld observed that whenever sulphur and ferrous sulphide are boiled together in neutral or feebly acidic soln., pyrite is formed. E. T. Allen and co-workers found that the first product of the action of hydrogen sulphide on a soln. of ferric sulphate can be represented by:  $\text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{S} = \text{S} + 2\text{FeSO}_4 + \text{H}_2\text{SO}_4$ , when the hydrogen sulphide is prevented from oxidation or escape—say, by confining the mixture in a sealed tube—a second reaction:  $\text{FeSO}_4 + \text{S} + \text{H}_2\text{S} = \text{FeS}_2 + \text{H}_2\text{SO}_4$ , occurs. The velocity of the latter reaction is slow at room temp., but faster at 200°. The product of the action at 200° for 2 days, is washed first with water, then digested with ammonium sulphide to remove the excess of sulphur, boiled with 20 per cent. hydrochloric acid, washed in an atm. of carbon dioxide, and dried in vacuo. Marcasite is the main product. Sulphuric acid is here a product of the reaction in which marcasite forms, and the concentration of the acid increases during the progress of the reaction. A greater initial concentration of acid favours the development of marcasite. Thus, with 5 grms. of ammonium ferrous sulphate, 100 c.c. of water saturated with hydrogen sulphide and,

Free $\text{H}_2\text{SO}_4$	0.50	0.57	0.78	1.18 grm.
Marcasite	57	75	90	92.5 per cent.
Pyrite	43	25	10	7.5 „

Working at different temp. with the same mixture, but with 0.17 grm. of free sulphuric acid, at 300°, 200°, and 100°, the products contained respectively 43, 68, and 92 per cent. of marcasite. This shows that the higher the temp., the greater is the proportion of pyrite. It was also observed that although a high concentration of acid favours the production of marcasite, there is for each temp. a certain critical conc. of acid which inhibits the reaction:  $\text{FeSO}_4 + \text{H}_2\text{S} + \text{S} = \text{FeS}_2 + \text{H}_2\text{SO}_4$ . This critical conc. of acid is smaller, the lower is the temp. It bears no relation to the solubility of the sulphide, for at room temp. the quantity is a fraction of 1 per cent., whereas at 200° it is between 3.5 and 5 per cent. during periods of a few weeks.

F. Wöhler heated marcasite and pyrite for 4 hrs. at about 445°, but observed no transformation of the one into the other, but the observations of E. T. Allen and co-workers showed that marcasite slowly changes into pyrite at this temp., and J. Königsberger and O. Reichenheim found a marked decrease in the electrical resistance of marcasite near 520° such that the resistance becomes of the same order as that of pyrite. They consider that their results prove that marcasite changes into pyrite, and that the change is irreversible. E. T. Allen and co-workers observed no evidence of any change at 300° and 350°, although

J. Königsberger and O. Reichenheim thought that the change begins between 250° and 300°. The heating curves, Fig. 628, show that between 500° and 600° marcasite undergoes a change which is accompanied by the evolution of heat.

A. Cavazzi considered that the heats of combustion of the two forms are the same, but in view of the heating curves, this can mean only that the method of measurement was not sensitive enough to detect a difference. The condition of instability of marcasite revealed by its possessing more energy, is in accord with the greater chemical activity of marcasite. For some unknown reason, monotropic forms often crystallize from some particular solvent, or within a limited temp. range, and the formation of marcasite in acidic soln. is an example of this. A rise of temp. hastens the monotropic reaction: marcasite  $\rightarrow$  pyrite; at low temp. it is immeasurably slow or zero; above 450°, it is fast enough to measure. Hence, it is possible that pyrite never changes to marcasite without first passing into soln., while the opposite change readily occurs.

H. V. Anderson and K. G. Chesley followed the change of marcasite into pyrite at 415° by observations on the X-radiograms. P. von Jereméeff, and J. R. Blum mentioned pseudomorphs of marcasite after pyrite, but E. T. Allen and co-workers' observations show that paramorphs of pyrite after marcasite are possible, but paramorphs of marcasite after pyrite are impossible.

Pyrite has a higher density than marcasite, and if H. le Chatelier's law—2, 17, 4—were applicable to irreversible changes, it should be possible to effect the transformation of marcasite to pyrite by pressure; but there is no warrant for assuming that press. favours all changes accompanied by a reduction in vol., irrespective of their reversibility. E. T. Allen and co-workers, however, found that no pyrite formation was observed when a few grams of marcasite were compressed for 5 hrs. at 10,000 atm. at ordinary temp., or when compressed at 2,000 atm. at 300° to 400°.

As just indicated, F. Wöhler obtained no evidence of the formation of marcasite by heating pyrite for 4 hrs. at 445°. Nor did C. Doelter succeed in synthesizing marcasite by heating a mixture of ferrous sulphate and carbon at a red-heat in a current of hydrogen sulphide, by the action of coal-gas and hydrogen sulphide on heated ferrous sulphate, or by the action of hydrogen sulphide on heated ferrous carbonate. He obtained twinned crystals of marcasite by treating ferrous sulphate with distilled water, with soda-lye, or with a soln. of sodium sulphide—but this has not been confirmed—*vide supra*. L. Michel reported that aggregates of what appeared to be rhombic marcasite were obtained as a by-product in synthesizing garnet, by heating in a graphite crucible at 1200° for 5 hrs. a mixture of titaniferous iron ore, calcium sulphide, silica, and carbon. The result has not been confirmed.

H. Schneiderhöhn,<sup>10</sup> F. V. von Hahn, and F. Bernauer observed specimens of marcasite which appeared to contain the **colloidal iron disulphide**, presumably marcasite; and the hydrogel found in Miocene clays of the Melnikoff Estates, Samara, Russia, was named **melnikoffite**, *melnikowite*, or *melnikovite*, by B. Doss. The hydrogel was examined by H. Ehrenberg. Hydrated iron disulphide was studied by M. P. Tschirvinsky, L. M. Jegunoff, J. Habermann, and K. Andrée; and B. Doss observed that it occurred in a number of different localities. W. Feld showed that the hydrogel of ferrous sulphide can be converted into the hydrogel of iron disulphide by the sequence of reactions:  $2\text{FeS} + 3\text{SO}_2 = 2\text{FeS}_2\text{O}_3 + \text{S}$ ;  $\text{FeS}_2\text{O}_3 + 3\text{H}_2\text{S} = 4\text{S} + 2\text{H}_2\text{O} + \text{FeS} \cdot \text{H}_2\text{O}$ ; and  $\text{FeS} \cdot \text{H}_2\text{O} + \text{S} = \text{FeS}_2 + \text{H}_2\text{O}$ . B. Doss observed that the colloidal melnikoffite may be regarded as a stage in the transformation of hydrotroilite into pyrite: Troilite gel  $\rightarrow$  melnikoffite gel  $\rightarrow$  melnikoffite  $\rightarrow$  pyrite. E. T. Allen and co-workers observed that when an alkali polysulphide acts on a soln. of ferric sulphate, the formation of amorphous iron disulphide

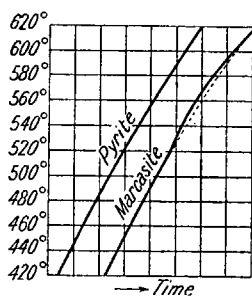


FIG. 628.—Heating Curves of Marcasite and Pyrite.

precedes the formation of pyrite ; J. D. Clark and P. L. Menaul found that crystalline pyrite is peptized by alkaline soln. in the presence of hydrogen sulphide ; and F. V. von Hahn obtained a hydrosol by spluttering from the pyrite arc under water ; if in a soln. of alkali-lye, the sol is very stable. Melnikoffite is black with a steel-grey lustre ; its sp. gr. is 4.2 to 4.3 ; and its hardness 2 to 3. K. C. Berz suggested that melnikoffite is a mixture of sulphide and oxide. When heated in a dry tube, sulphur is sublimed. With boiling water, it is hydrolyzed forming ferrous sulphide and sulphur, while, according to L. Benedek, pyrite suffers this transformation between 300° and 400°. B. Doss represents the reaction :  $\text{FeS}_2 = \text{FeS} + \text{S}$ , and  $\text{FeS} + 2\text{H}_2\text{O} = \text{Fe}(\text{OH})_2 + \text{H}_2\text{S}$ . Melnikoffite is insoluble in water. Potash-lye decomposes the mineral to form orange-red hydrated ferric oxide. An alkaline soln. of bromine-water decomposes melnikoffite rapidly, whilst J. Lemberg found that pyrite is decomposed only slowly. A 10 per cent. soln. of iodine and potassium iodide strongly attacks melnikoffite. Dil. hydrochloric acid at ordinary temp. attacks it slowly, but when warmed, iron passes into soln., and a skeleton of sulphur remains. The mineral is peptized by a soln. of hydrogen sulphide, and likewise by a 10 per cent. soln. of sodium sulphide—note A. Terrell's and C. Doelter's experiments on pyrite—*vide infra*. Hot acetic acid has only a slight attack on the mineral ; but it is dissolved by warm nitric acid. A soln. of potassium cyanide rapidly converts melnikoffite into soluble ferrocyanide, but pyrite under the same conditions is only slightly attacked.

**The physical properties of pyrite.**—Pyrite occurs in crystals or aggregates of crystals, and frequently in fine or granular masses. It sometimes occurs in radiating fibrous masses, in reniform or globular nodules, as well as stalactitic. The **colour** on fresh surfaces is nearly uniform, pale brass-yellow, and the streak is greenish-black or brownish-black. According to J. L. C. Schroeder van der Kolk,<sup>11</sup> the streak is pale brown to pale violet. H. du Bois observed pleochroism with a polished surface of the crystal ; J. Königsberger studied the pleochroic reflection ; and E. P. T. Tyndall observed no change in the reflecting power at low temp.

J. B. L. Romé de l'Isle, R. J. Haüy, A. G. Werner, and N. Steno showed that the many forms in which the **crystals** occur can be all derived from the cube, and that the crystals belong to the cubic system. E. T. Allen and co-workers found that the artificial crystals of pyrite show both the cubic and the octahedral faces, but both forms occur alone ; pyritohedra were not observed. The faces were always warped and imperfect. The angles were close to the theoretical values. The isomorphism of pyrite with iron, nickel, and cobalt sulphoarsenides was discussed by C. F. Rammelsberg. The crystals of pyrite exhibit various forms of **twinning**. The twinning is that characteristic of penetration twins with parallel axes. The apparently simple crystals may really be supplementary twins. Even when the crystals occur in simple cubes the symmetry of the twinning is revealed by the well-marked striations which are parallel to alternate pairs of edges, so that the striations on these faces are at right-angles to those on the adjacent faces. The repetition of minute crystal faces, by what is called an oscillatory combination, sometimes tends to produce rounded faces. The faces of the octahedral forms are generally smooth and bright. The pentagonal dodecahedron is so characteristic of the crystals of pyrite, that the form is sometimes called the *pyritohedron* ; while the dodecahedron is comparatively rare. The crystals are sometimes abnormally developed so that they are rod-like or acicular owing to their elongation in the direction of a cubic axis ; and the crystals may be abnormally developed with tetragonal or rhombic symmetry. In the so-called supplementary twinning, one crystal appears to project entirely through the other. Some pyritohedral crystals have their faces striated parallel to the cubic edges, and others have their faces striated perpendicular to those edges ; the former are thermoelectrically positive to copper, and the latter, negative. Some crystals of pyrite are partly positive and partly negative.

The various crystal forms of pyrite were described by A. d'Achiardi, G. B. d'Achiardi, C. Arevalo, A. Arzruni, E. F. Ayres, V. L. Ayres, F. Azzini, F. A. Bannister, M. Bauer, F. Becke, J. Beckenkamp, G. Boeries, A. Breithaupt, A. Brezina, W. C. Brögger, A. Brunlechner, M. J. Buerger, L. Busatti, H. Buttgenbach, A. Cathrein, G. Cesaro, K. Chudoba, J. H. Collins, L. Colomba, J. D. Dana, E. Doll, C. Doelter, C. Düsing, H. Ehrenberg, J. Eyerman, G. Flink, A. Franzenau, A. Franzenau and L. Tokody, A. Frenzel, P. Gaubert, F. A. Genth, E. Glatzel, V. Goldschmidt and co-workers, G. Greim, H. F. Grondijs and C. Schouten, P. Groth, G. Häag and I. Sucksdorf, E. Hatle, A. C. Hawkins, R. Helmhacker, C. Hintze, W. H. Hobbs, H. Höfer, E. Hussak, S. Ichikawa, P. von Jereméeff, K. Jimbo, G. Kalb, G. A. Kenngott, N. von Kokscharoff, J. Krenner and K. Zimanyi, A. Lacroix, H. Laspeyres, G. Leonhard, A. Liffa, A. Liveridge, M. Löw and co-workers, G. Lowe, O. Lueddecke, A. Martelli, B. Mauritz, L. Maros, W. J. Mead and C. O. Swanson, R. Meli, H. Miers, L. Miropolsky, A. J. Moses, O. Mügge, L. F. Navarro, P. Niggli, A. E. Nordenskjöld, C. Palaché and H. O. Wood, U. Panichi, R. L. Parker and W. O. Kennedy, S. L. Penfield, L. S. Ramsdell, G. vom Rath, R. Reinicke, J. W. Retgers, P. y Rico, A. F. Rogers, G. Rose, V. Rosicky, A. Sadebeck, J. Samojloff, F. Sandberger, F. Sansoni, E. Scacchi, F. Scharff, C. Schmidt, E. Schnaebele, W. B. Smith, G. Smolar, L. J. Spencer, A. Stelzner, G. Striiver, E. Tacconi, L. Tokody, F. D. Tosas, H. Traube, C. Travis, R. Tronquoy, G. Tschernak, P. Tschirwinsky, G. H. F. Ulrich, T. Wada, M. Websky, E. Weinschenk, H. P. Whitlock, F. J. Wiik, G. H. Williams, D. F. Wiser, K. Zerrenner, K. Zimanyi, etc.

The **cleavages** (100) and (111) are indistinct. The **corrosion figures** were investigated by A. Johnsen, V. Pöschl, F. Becke, E. H. Kraus and J. D. Scott, E. Thomson, B. Granigg, M. Leo, J. Lemberg, S. Ichikawa, L. Tokody, G. Tammann and W. Krings, G. Rose, and H. Schneiderhöhn. S. Ichikawa noted that the symmetry of all etching figures corresponds with the hemihedral symmetry of the crystals. The pits and striations are closely related. The pits on pyrite crystals, with natural etchings, are accompanied by striations on the same faces. If the etching progresses farther, eye-shaped pits are produced with a centre of tetragonal pyramidal form at the extremities of the binary hemihedral axis of symmetry so that the etched crystal is modified to a cube-like form, then gradually modified to a tetrahedral form, and is at last wholly dissolved away. M. Watanabe found that the cube faces of pyrite are corroded about 1.3 times quicker than the octahedron faces. The **gliding-plane**, (121), was noted by G. Smolar, but this has not been confirmed. K. Veit studied the subject. The microscopic appearance of polished sections was described by A. A. Julien, B. Granigg, F. N. Guild, and H. Schneiderhöhn. K. Veit, F. D. Adams, and M. J. Buerger studied the deformation of the crystals by pressure.

W. L. Bragg studied the **X-radiograms** of pyrite, and the results were in agreement with the assumption that the iron atoms are arranged in a face-centred

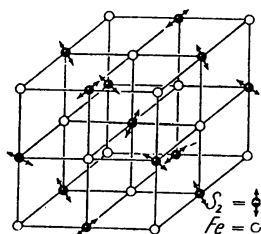


Fig. 629.—Space-lattice of Pyrite.

lattice; and, if a series of non-intersecting three-fold axes are chosen, one passing through each iron atom, so that each small cube has a single diagonal which is a three-fold axis of symmetry. Each cube contains one sulphur atom which lies on the diagonal near the empty corner, and divides the diagonal in the ratio 1:4. P. Niggli represented the lattice by Fig. 629, in accord with the scheme for closest packing. The simple formula of pyrite is taken to be in accord with that of J. Loczka, and in the diagram the black dot is considered as the centre of gravity of the  $S_2$ -atoms. In that case, the space-lattice resembles that for sodium

chloride. J. W. Gruner said that the S-S radicles in pyrite can be compared to dumb-bells whose axes are parallel to the three-fold cubic axes. The radicles are so distributed that each octant of unit cube contains half a radicle; but the axes of adjoining radicles (which are less apart than the length of the edge of unit cube) are not parallel. Each S-atom of the radicle forms the corner of three tetrahedrons which are symmetrical with respect to the three-fold axis in which the radicle lies. These slightly distorted tetrahedra are linked

to other sets of tetrahedra directly, as well as by means of radicles. This arrangement cannot well be shown in a two-dimensional diagram. The centres of gravity of the dumb-bells are in the positions of face-centred cubes, and, therefore, the radicles are in a close-packing. This gives a very dense structure for pyrite. Zinc blende has a unit cell nearly the same size as pyrite, and each cell contains four molecules, but pyrite has twice as many atoms of sulphur in the same volume. E. Onorato found both the (210)-spacings are equal to 2.406 Å.; R. Juza and W. Biltz observed no evidence of intermediate forms in the reaction:  $\text{FeS}_2 \rightarrow \text{FeS} + \text{S}$ —*vide infra*. The structure of the space-lattice has been also discussed by H. V. Anderson and K. G. Chesley, A. Reis, M. L. Huggins, F. Haag, R. Scharizer, N. H. Kolkmeijer, P. F. Kerr, F. R. and K. R. van Horn, and J. Beckenkamp. P. P. Ewald and W. Friedrich calculated the density to be 5.38, the side of the elementary cube  $a = 5.40 \times 10^{-8}$  cm.; the distance between two iron atoms in the direction (110) is  $3.82 \times 10^{-8}$  cm.; the distance between the two sulphur atoms of the  $\text{S}_2$ -complex, in the direction of the trigonal axis, (111), is  $2.06 \times 10^{-8}$  cm., which is closer than it is in other known sulphides; and the distance of the centre of gravity of the  $\text{S}_2$ -complex from the centre of gravity of the iron atom is  $2.70 \times 10^{-8}$  cm. in the direction of the (001)-face. H. M. Parker and W. J. Whitehouse gave for the spacing of the cell, 5.405 Å.; for the distance between the centres of adjacent sulphur atoms, 2.14 Å.; and between adjacent sulphur and iron atoms, 2.26 Å. R. von Nardroff calculated for the density, 5.40560; and I. Oftedal, 5.414. M. L. Huggins studied the effect of the space-lattice structure on the properties of pyrite; P. Niggli, the electronic structure; J. R. Tillman, the inner potential; and J. Forrest, the magnetic lattice.

Numerous observations have been made on the **specific gravity** of pyrite. G. A. Kenngott found values ranging from 4.807 to 5.028; V. Pöschl, 5.169 to 4.903; A. Breithaupt, 4.960 to 5.158; F. E. Neumann, 5.042; A. S. Herschel and G. A. Lebour, 4.66; E. Madelung and R. Fuchs, 4.9803; H. N. Stokes, 5.041 to 4.563; J. D. Dana, 4.95 to 5.10; J. Samojloff, 4.990; E. C. Schiffer, 5.016; C. F. Rammelsberg, 4.826 to 4.919—best representative value 5.00; A. A. Julien, 5.01; F. Kollbeck, 4.85 to 4.95; and C. U. Shepard, 4.863. According to E. T. Allen and co-workers, the sp. gr. of artificial pyrite is 5.02, which is very near the value of pyrite from Elba; and V. Rodt gave 4.588 at  $18^\circ/4^\circ$ . F. Gieseler gave 4.838 at  $25^\circ/4^\circ$  for the sp. gr. of the synthetic disulphide; and calculated 24.8 for the mol. vol., and 8.9 for the at. vol. of the contained sulphur. This means a contraction of 41.4 per cent. during the formation of the compound. R. Juza and W. Biltz observed the sp. gr. at  $25^\circ/4^\circ$  and mol. vol.:

FeSn . . .	1.942	1.907	1.720	1.450	1.345	1.187	1.118	1.068	1.028
Sp. gr.. . .	4.978	4.975	4.896	4.769	4.725	4.605	4.593	4.637	4.736
Mol. vol. . .	23.7	23.5	22.7	21.4	20.9	20.4	19.95	19.4	18.7

and the results are plotted in Fig. 630. The results of the X-radiograms are indicated at the bottom. W. H. Goodchild, J. J. Saslawsky, N. S. Kurnakoff and S. F. Schemtschuschny, and I. Maydall also calculated values for the vol. contraction which occurs during the formation of pyrite from its elements; and F. J. Malaguti and J. Durocher attempted to correlate the sp. gr. with the crystalline form, but neither G. A. Kenngott nor A. A. Julien thought there was any good reason for adopting the suggestion. The **hardness** of pyrite is between 6 and 6.5; A. A. Julien gave 6.51. Pyrite is one of the hardest of the sulphide minerals. Iron pyrites is so hard that it will take a good polish, and some is used for cheap jewellery, when it is cut in the form of a flat rosette. Polished plates of pyrite have been found in the

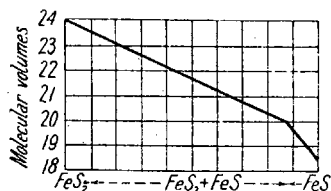


FIG. 630.—Molecular Volumes of the Iron Sulphides.

graves of the Incas of ancient Peru, and they are now known as *Incastones*; they are thought to have been used as mirrors. F. Pfaff gave 58 for the boring hardness of pyrite on the (100)-face when that of talc is unity. According to V. Pöschl, the scratching hardness of pyrite is 182.2 and 199.1 respectively under loads of 20 and 50 grms. when the hardness of topaz is 1000; and with one and the same face, the hardness does not vary with the direction of scratching. The hardness of different faces of one and the same crystal is the same when the surface conditions are constant, differences occur when there is a change in the structure. C. Viola discussed the cohesion of the crystals; and although G. Smolar regarded (12 $\bar{1}$ ) as a gliding plane, O. Mügge observed no change under a press. of 35,000 atm., but cleavage on the (001)-face appeared. Pyrite, at ordinary temp., is very resistant towards high press. F. D. Adams found that under a compression of 43,000 lbs. applied in 17 minutes, pyrite crushed to powder without showing any signs of plastic deformation, but M. J. Buerger obtained evidence of the phenomenon. W. Voigt measured the **elastic constants** of pyrite, and found for the elastic modulus 35,300 kgrms. per sq. mm. in the direction of a cubic face, and 25,300 kgrms. per sq. mm. in the direction of the rhombic dodecahedron face, the torsion modulus in the direction of surface is 10,750 kgrms. per sq. mm., and the compressibility is 0.000114 kgrm. per sq. mm. F. D. Adams gave  $0.70 \times 10^{-6}$  for the **compressibility** of pyrite; P. W. Bridgman gave  $0.6728-1.95 \times 10^{-12}$  at 30°, and  $-0.6716-1.95 \times 10^{-2}$  at 75° for press. up to 12,000 kgrms. per sq. cm.; L. H. Adams and E. D. Williamson found the coeff. of compressibility of pyrite to be  $\beta = 0.71 \times 10^{-6}$  for press. ranging from 0 to 10,000 megabars; and for  $d\beta/dp$ , L. H. Adams gave  $-0.0_{11}4$ ; whilst E. Madelung and R. Fuchs obtained  $\beta = 0.0_{61}7$ ; and W. Voigt,  $\beta = 0.0_{51}13$ . L. Hopf and G. Lechner gave for the **velocity of sound** in absolute units,  $5.43 \times 10^5$ ; and A. Eucken,  $5.020 \times 10^5$ .

According to H. Fizeau,<sup>12</sup> the coeff. of **thermal expansion** of pyrite at 40° is  $\alpha = 0.000009071$  when taken at right-angles to a natural face of the cube, and 0.00000908 when taken in a group of crystals, without reference to any common direction. F. Pfaff gave 0.000010084 for the linear coeff. between 0° and 100°; H. Kopp gave 0.000034 for the coeff. of cubical expansion between 15° and 47°. S. Valentiner and J. Wallot observed that between -25.2° and 18.5°, the linear coeff.  $\alpha = 0.0_{58}43$ ; between -46.2° and -25.2°,  $0.0_{57}73$ ; between -70.5° and -46.2°,  $0.0_{57}09$ ; between -131.9° and -104.3°,  $0.0_{55}16$ ; between -154.9° and -131.9°,  $0.0_{53}92$ ; and between -175.2° and -154.9°,  $0.0_{52}95$ . The subject was studied by E. Grüneisen. H. de Sénarmont found the **thermal conductivity** of pyrite to be large. F. E. Neumann found the **specific heat** of pyrite to be 0.1267 to 0.1279; A. de la Rive and F. Marcet gave 0.1396; A. S. Herschel and G. A. Lebour, 0.125; H. V. Regnault, 0.1301 between 14° and 100°; H. Kopp, 0.1230 to 0.1238 between 18° and 47°; J. Thoulet and H. Lagarde, 0.13029; J. Joly, 0.1301 to 0.1306 between 12° and 100°; A. Sella, 0.1460; S. Pagliani, 0.1295 between 20° and 100°; and K. Bornemann and O. Hengstenberg, 0.1284 between 0° and 100°, and 0.1290 for a sample with 1 per cent. of SiO<sub>2</sub>. K. Försterling calculated values from the elastic constants and the vibration frequency; and I. Maydell studied the mol. ht. A. Eucken and F. Schweser gave for the sp. ht. between -189.1° and -251.4°, and R. Ewald, between -135° and 28°—the full collection is given by H. Miething:

	28°	-38°	-135°	-189.1°	-216.2°	-243.0°	-251.4°
Sp. ht.	0.1219	0.1087	0.0640	0.0259	0.0079	0.0012	0.00054
Mol. ht.	14.64	13.04	7.63	3.11	0.952	0.139	0.0648

According to H. Rose, J. J. Berzelius, B. G. Bredberg, and C. F. Rammelsberg, when pyrite is heated not very strongly in a closed vessel, it dissociates with the evolution of sulphur, and at a higher temp. passes into ferrous sulphide (*q.v.*); and, according to J. L. Proust, the residue retains the form and colour of the original pyrites, though it is more bulky. The product is dull, and exhibits surface

cavities formed by local fusion, and it may be crumbled to pieces when squeezed between the fingers. F. Fouqué and A. Michel-Lévy added that the product is pulverulent and not crystalline. The **thermal dissociation** of pyrite into pyrrhotite and sulphur vapour was studied by E. T. Allen and co-workers, and A. F. Gill

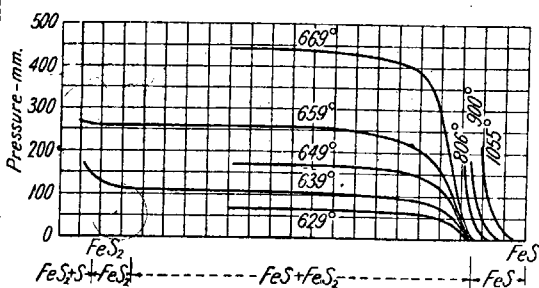


FIG. 631.—The Vapour Pressures of Decomposing Iron Disulphide.

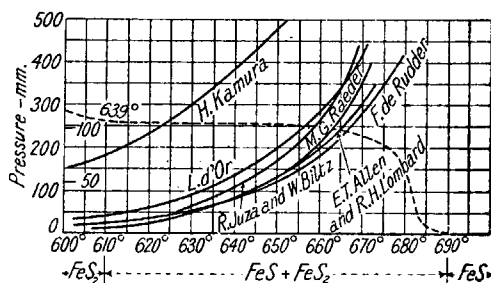


FIG. 632.—The Vapour Pressures of Pyrites.

—*vide supra*. E. Arbeiter observed that sulphur distils off when the pyrite is heated in vacuo. O. Mügge discussed the thermal contact metamorphosis of pyrites in clay shales, etc.; and W. Eitel, the passage of pyrite into pyrrhotite. G. Tammann and G. Bätz observed a break in the heating curve at 684° due to the loss of sulphur. E. T. Allen and co-workers found that the dissociation proceeds slowly at about 575°, and rapidly at 657° to form  $\text{FeS}(\text{S})_n$ ; and this in an atm. of sulphur when the **dissociation pressure** is 1 atm. at 689°. W. Hempel and C. Schubert, and C. Schubert said that dissociation begins at 480°, and is ended above 1400°; and E. Kothny, that dissociation begins at 200°, and at 700°, in an inert gas,  $p=1$  atm.; O. Barth found the dissociation begins at 350°, and when air is excluded,  $p=1$  atm. at 600°; and J. Joly, at 450°. C. Schubert measured the dissociation press., and L. H. Bergström found the dissociation temp. to be 800°, at 40 to 60 atm. press. E. T. Allen and R. H. Lombard represented their observations on the dissociation press.,  $p$  mm., by  $\log p = -191942 \cdot 61 T^{-1} - 434 \cdot 195075 \log T + 1497 \cdot 56707$ ; the observed results were:

	575°	595°	610°	625°	645°	665°	672°	680°	689°
$p$	0.75	3.5	13.5	36.3	106.5	251	243	518	760

The results are plotted in Fig. 633. L. d'Or found the partial press.,  $p$  mm., of  $\text{S}_2$  is related to the absolute temp. between 548° and 676° by  $\log p = -13 \cdot 380 T^{-1} + \log T + 13 \cdot 8205$ . The observed and calculated results were:

		601°	619°	654°	664.5°	670°	676°
$p$	Calc.	28.5	(59)	226	331	408	500
	Obs.	30	59	223.5	333.5	413	504.5

The partial press.,  $p$ , of the sulphur in its different forms were:

		548°	601°	619°	637°	654°	676°
$p$	$\text{S}_2$	2.8	30	59	119	223.5	504.5
	$\text{S}_6$	0.001	0.14	0.5	1.95	6.65	32.5
	$\text{S}_8$	0.001	0.002	0.01	0.157	0.25	2.9

A. C. Halferdahl gave  $\log p = -9912 \cdot 09 T^{-1} + 29 \cdot 8543 \log T - 757084$ . M. G. Raeder gave for the dissociation press.,  $p$  mm.,  $\text{FeS}_2 = \text{FeS} + \text{S}$ :

		580°	612°	637°	651°	663°	672°	680°	686°
$p$		2.8	22	73	140	250	393	575	772

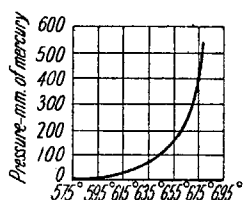


FIG. 633.—The Dissociation Pressure of Pyrite.



G. Marchal observed that the dissociation of pyrite in vacuo begins at  $500^{\circ}$ ; it is rapid at  $550^{\circ}$ ; and is completed in 8 hrs. at  $670^{\circ}$  to  $680^{\circ}$ , or in 2 hrs. at  $850^{\circ}$ . At  $1200^{\circ}$ , the residue is a mixture of ferrous sulphide and a little iron. Dissociation is very rapid in an atm. of nitrogen at  $850^{\circ}$ . R. Juza and W. Biltz's results are summarized in Fig. 632. The dotted curve and inner ordinates refer to the vap. press. of iron disulphide at different temp. The results of the observations on the X-radiograms are indicated at the bottom. Observations were also made by H. Kamura, F. de Rudder, and M. G. Raeder (Fig. 631). The results of W. F. de Jong and H. W. V. Willems, by X-radiograms, and of L. d'Or, by absorption spectra, show that the dissociation is a reversible reaction involving only two solid phases,  $\text{FeS}$  and  $\text{FeS}_2$ . C. Fontana thought that  $\text{Fe}_3\text{S}_4$  exists, but the X-radiograms show no evidence of this.

R. Cusack said that the **melting-point** of pyrite is  $642^{\circ}$ ; J. Joly gave  $450^{\circ}$ ; but, according to L. Benedek, when pyrite is heated to redness in an inert atm., say of carbon dioxide, it loses half its sulphur to form ferrous sulphide, and a similar result is obtained at  $300^{\circ}$  to  $400^{\circ}$  in an atm. of steam. Hence, pyrite decomposes before it reaches the m.p. J. Baumann calculated the **temperature of combustion** or the temp. of the flame produced by burning pyrite:  $2\text{FeS}_2 + 11\text{O} = \text{Fe}_2\text{O}_3 + 4\text{SO}_2$ , and found  $1216^{\circ}$ ; this value is scarcely half as great as that given by F. Bode. J. S. Doting obtained  $965^{\circ}$ ; and F. de Rudder and M. Ferrer pointed out that the temp. is smaller if pyrite be taken as  $\text{FeS}_2$  rather than as  $\text{FeS} + \text{S}$ . A. Cavazzi gave for the **heat of combustion** or **oxidation** of pyrite, 1.55 Cals. per gram; W. H. Emmons, 2.7 Cals.; and E. E. Somermeier, 1.557 Cals. E. T. Allen and R. H. Lombard did not succeed in calculating satisfactory values for the heat of dissociation from the observed dissociation data because of the change in the density of sulphur vapour with press., and on account of the variation in the composition of the solid phase, pyrrhotite. H. Kamura calculated from the observed absorption of heat, the **heat of formation** ( $\text{FeS}, S_{\text{gas}}$ ) = 18.611 Cals.; W. G. Mixter observed ( $\text{FeS}_{\text{amorphous}}, S_{\text{gas}}$ ) =  $\text{FeS}_{2\text{cryst.}} + 16.7$  Cals.; or ( $\text{Fe}_2\text{S}$ ) = 35.5 Cals. F. de Rudder and M. Ferrer gave ( $\text{FeS}, S_{\text{gas}}$ ) = 18.513 Cals.; and H. Kamura, 18.611 Cals. L. d'Or gave  $2\text{FeS}_2 = 2\text{FeS} + \text{S}_2 - 61$  Cals., and the energy of fixation of the first sulphur atom is 90.5 Cals., and that of the second, 82.5 Cals. For sulphur in the gaseous form, the values calculated for the heat of formation are: ( $\text{FeS}, \frac{1}{2}\text{S}_2$ ) = 30.5 Cals.; ( $\text{FeS}, \text{S}$ ) = 81.5 Cals.; ( $\text{Fe}, \text{S}_2$ ) = 69.5 Cals.; and ( $\text{Fe}, 2\text{S}$ ) = 171.5 Cals. F. de Rudder gave 18.518 Cals. for the heat of dissociation. A. C. Halferdahl found the heat of decomposition of pyrites to a solid soln. of ferrous sulphide and sulphur, to be  $-10$  Cals. at  $575^{\circ}$  to  $680^{\circ}$ . He also gave, at room temp.,  $7\text{FeS}_2 \rightarrow \text{Fe}_7\text{S}_8 + 3\text{S}_2 - 8910$  cal.; and at  $625^{\circ}$ ,  $2\text{FeS}_2 \rightarrow 2\text{FeS} + \text{S}_2 - 34,260$  cal. K. K. Kelley studied the **entropy**.

The **index of refraction** for X-rays calculated by R. von Nardroff,<sup>13</sup> B. Davis and R. von Nardroff, and B. Davis was found to be  $3.35 \times 10^{-6}$  for  $\text{MoK}\alpha$ -rays, and

$2.87 \times 10^{-6}$  for the  $\text{MoK}\beta$ -rays; and  $17.6 \times 10^{-6}$  for the  $\text{CuK}\alpha$ -rays, and  $13.2 \times 10^{-6}$  for the  $\text{CuK}\beta$ -rays. W. W. Coblentz measured the ultra-red **reflecting power** of pyrite, and found that it gradually increased from 25 per cent. at  $2\mu$  to 34 per cent. at  $12\mu$ —hatched line, Fig. 634. The low reflection at  $2\mu$  was attributed to lack of polish since another sample had a constant reflecting power

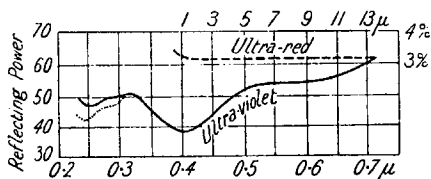


FIG. 634.—The Reflecting Power of Pyrite.

from  $3\mu$  to  $14\mu$  of about 32 per cent. He also found the curve for the ultra-violet reflecting power to be that indicated in Fig. 634, which coupled up the observations of E. P. T. Tyndall. The effect of ageing on the optical properties of the surface in the region 240 to 320  $m\mu$  is shown by the dotted line, Fig. 634. The subject was studied by J. Königsberger and co-workers, and W. Ehrenberg and co-workers.

A. de Gramont studied the **spark spectrum**; and G. E. Claussen, the spark and **arc spectrum**. C. Doelter found that pyrite is opaque to the **X-rays**; H. Raether studied the action of canal rays; and K. R. Dixit, the potential of pyrites for electronic diffraction. G. A. Lindsay and H. R. Voorhees, and S. Tanaka and G. Okuno studied the X-ray absorption spectrum; B. Davis and R. von Nardroff, the refraction of the X-rays; P. de la Cierva and J. Losada, the reflection of X-rays; O. Stelling, the absorption of X-rays; and H. Raether, the diffraction of electrons. J. O. Perrine found that no fluorescence is produced in ultra-violet rays. A. Pochettino observed that pyrite shows a bluish-green **cathodoluminescence**; and J. Calafat y Léon, a violet **thermoluminescence** when the powder is strewn on a hot, but not red-hot, metal plate; A. Karl studied the **triboluminescence**. A. Rohde found that the **photoelectric effect** with pyrite is greater than that of pyrrhotite or of marcasite. A. Meissner found that when pyrite, in an electric field of 1000 to 2000 volts, is heated to 135°, there is produced a **pyroelectric effect** of 3·7 volts. F. Kirchner and H. Raether studied the dispersion of cathode rays by the crystal. M. von Laue and E. Rupp observed no difference in the electron diffraction from different faces of the crystals. P. Gaubert, E. T. Wherry, A. Schleede and H. Buggisch, J. N. Frers, and H. S. Roberts and L. H. Adams studied its use as a **radio-detector**.

R. J. Haüy<sup>14</sup> observed that when pyrite is rubbed with a piece of cloth, the **frictional electricity** is negative. H. F. Vieweg studied the subject. F. Beijerinck, and R. G. Harvey found that the **electrical conductivity** of pyrite is good. J. Königsberger and O. Reichenheim gave 0·00381 mercury unit for the sp. conductivity of pyrite at 20·5°; H. Löwy obtained a higher value. The **electrical resistance** of pyrite at 40° is 1·282 ohms, when that of marcasite is 239·5 ohms. Observations were made by J. Pelletier, R. W. Fox, F. Braun, E. van Aubel, A. Abt, C. Bedel, J. F. L. Hausmann and F. C. Henrici, M. Faraday, W. Skey, H. Dufet, and H. Meyer. O. Reichenheim, and K. Baedeker gave 0·024 ohm for the sp. resistance at 0°; and J. Königsberger and co-workers found that the conductivity of pyrite is 500 times that of marcasite, and that the electrical resistance,  $R$ , of pyrite, parallel to the  $b$ -axis, and at  $\theta^\circ$ , can be represented by  $R=0\cdot0240(1+0\cdot00385\theta+0\cdot000037\theta^2)_e-240/(\theta+273)273$ . The observed results are:

	-78°	20°	85°	121°	260°	340°
$R$	0·0251	0·0240	0·0279	0·0300	0·0357	0·0388

Hence, the resistance increases slowly up to about 350°, and then reverses. The transition point corresponds with P. Weiss' abrupt fall in the ferromagnetism. It is assumed that an allotropic modification forms between 300° and 400°. According to J. Königsberger and K. Schilling, the absolute electrical resistance per c.c. of a very pure sample of native iron sulphide,  $\text{FeS}_2$ , perpendicular to the  $c$ -axis, fell from 0·000802 at -189° to 0·000256 at 277°, and 0·000262 at 310°, and at higher temperatures, the resistance increases a little. The electrical resistance, measured parallel to the  $c$ -axis, falls from 0·00107 at -188° to about 0·000387 at 350°, and this represents the range of stability of what is called  **$\alpha$ -pyrites**; the resistance rises from 0·000380 at 350° to 0·000375 at 445°. Above the transition point, 348°-350°, the stable form is called  **$\beta$ -pyrites**. The transition point for the electrical resistance corresponds with P. Weiss' abrupt fall in the ferromagnetism at about 348°. B. Beckmann gave 0·00294 for the sp. resistance in ohms at 0°, and observed that the ratio  $R:R_0=1\cdot063$  at 15·8°, and 0·390 at -258°; or:

	100·9°	54·2°	44·5°	14·6°	0°	-78·6°	-193°
$R$	0·1437	0·1235	0·1192	0·1070	0·1010	0·0733	0·0513 ohm.

In the vicinity of 0°,  $R=R_0(1+0\cdot00353\theta+0\cdot0\cdot56\theta^2)$ . A. Wesely, F. Streintz and co-workers, and J. Königsberger and co-workers, emphasized the increase in the resistance produced by surface films. The minimum observed in the resistance curve by J. Königsberger at -10° was not confirmed by B. Beckman; nor did

A. Wesely confirm J. Königsberger's observations of a decrease in the resistance at 360°. F. Streintz and A. Wesely gave 0.0023 to 0.0035 for the temp. coeff. of the resistance; and B. Beckman gave 0.00353 at 0°, and he represented the resistance as a function of the temp. by  $R = R_0 e^{a\theta}$ , where  $R$  is the resistance at  $\theta^\circ$ ;  $R_0$  the resistance at 0°; and  $a$ , the temp. coeff. B. Beckmann found that:

	-19.3°	-78.6°	44.5°	54.2°	100.9°
$R : R_0$	0.508	0.726	1.180	1.223	1.422

F. Streintz and A. Wellik observed that press. exerts a marked influence on the results; and B. Beckman gave for the effect of pressure,  $p$  atm., when  $R = 0.1010$  ohm,

$\frac{p}{\delta R/R}$	770	1255	1860	2390	2550
	0.0182	0.02915	0.04215	0.05305	0.05720

P. Collet observed a residual e.m.f. opposed to the current through the crystal, and the polarization effect may be referred to thermoelectric phenomena. C. W. Heaps found that the resistance is not influenced by a magnetic field. J. Königsberger and co-workers, and C. Doelter made observations on the theory of the electrical conductivity of pyrite. K. Fischbeck studied the electrolytic resistance of pyrites; and S. Borowik, the electrolytic valve action.

T. J. Seebeck made some observations on the **thermoelectric force** of pyrite; and W. G. Hankel found that the thermoelectric force of the (110)- or the (111)-face of pyrite towards copper is positive, whilst the (210)-face is partly positive and partly negative. H. Marbach also found some crystals of pyrite are positive, others negative; and A. Schrauf and E. S. Dana observed that most of the samples of pyrite which they examined were negative towards copper. The subject was examined by G. Strüver, H. Sutton, M. Kimura and co-workers, and K. Baedeker. G. Rose supposed that there is a relation between the hemihedry of the crystals of pyrite and their thermoelectric behaviour, but C. Friedel considered that this has not been established; the subject was discussed by J. Curie, J. Stefan, and J. Beckenkamp. W. Ogawa found that a current of 13,000 $\mu$  volt was developed with a couple of copper and pyrite. A. M. Iljef found that a cylinder of compressed powder of pyrite between two copper electrodes gives a thermoelectric current flowing in the direction of the fall of temp. J. Königsberger and J. Weiss observed a thermoelectric force of 0.000129 volt between 20° and 80°; and 0.000200 volt at 50°, where the current flowed from the pyrite to the copper. A. Abt examined the thermoelectric force between pyrite and chalcopyrite. W. H. Eccles studied the Peltier effect. E. T. Wherry found pyrite is a good **radio-detector**; and the subject was discussed by W. Ogawa, A. C. Hawkins, P. Glaubert, F. Frey, A. Schleede and H. Buggisch. J. N. Frers studied the system  $\text{FeS}_2\text{-PbS}$ ;  $\text{FeS}_2\text{-Pt}$ , and  $\text{FeS}_2\text{-ZnO}$ .

W. Skey found that in sea-water, the **electromotive series** of the sulphides is:  $\text{FeS}$ ,  $\text{MnS}$ ,  $\text{ZnS}$ ,  $\text{SnS}_2$ ,  $\text{HgS}$ ,  $\text{Ag}_2\text{S}$ ,  $\text{PbS}$ ,  $\text{Cu}_2\text{S}$ ,  $\text{FeS}_2$ ,  $\text{Sb}_2\text{S}_3$ , so that pyrite is positive towards galena. R. C. Wells found that the **electrode potential** of pyrite in  $N\text{-KCl}$  is 0.90 volt; in  $N\text{-H}_2\text{SO}_4$ , 0.95 volt; in  $N\text{-NaOH}$ , 0.14 volt; and in  $N\text{-Na}_2\text{S}$ , -0.17 volt. K. R. Dixit studied the inner potential; and H. B. Bull and co-workers, the electrokinetic potential. M. E. Conrad found that the **electromotive force** of pyrite is positive and of zinc negative in soln. of potassium or sodium hydroxide, and sulphuric acid, and R. Zuppinger found the effect is diminished by a rise of temp. V. H. Gottschalk and H. A. Buehler gave for the e.m.f. in volts of the minerals against copper in distilled water: marcasite, 0.37; chalcopyrite, 0.18 to 0.30; pyrite, 0.18; bornite, 0.17; hæmatite, 0.08 to 0.26; stibnite, -0.17 to 0.6; and zinc -0.83. A. Lipschitz and R. von Hasslinger found pyrite positive against a calomel electrode with an electrolyte of sulphuric acid with and without ferrous and ferric sulphates. V. H. Gottschalk and H. A. Buehler found that the potential of pyrite against copper in distilled water is 0.18 volt; and that with pyrite and galena in distilled water, the

pyrite is not attacked, and the galena is attacked; with sphalerite in place of galena, the sphalerite is attacked. R. C. Wells found that in the cell pyrite |  $N\text{-Fe}_2(\text{SO}_4)_3$  (acidified) | sodium sulphide | pyrite, the e.m.f. after 0.1, 1.0, 5.0, and 10.0 min. were respectively 1.04, 1.02, 1.00, and 1.00 volt. G. Tammann found that with pyrite against  $4N\text{-ZnSO}_4$  and zinc, the e.m.f. was 1.26 volt; against a sat. soln. of lead chloride and lead, 0.65 volt;  $2N\text{-CuSO}_4$  and copper, 0.20 volt; and a sat. soln. of silver sulphate and silver, 0.03 volt. G. N. Libby found that a pyrite anode in a cell of the Bunsen type gave twice the voltage of a cell with zinc blende as anode. A. Matsubara and J. Takubo studied the cathodic behaviour of pyrite.

K. G. Emeléus and J. W. Beck found the normal cathode fall of potential of iron pyrites, in volts, in:

Volts	Argon	Neon	Nitrogen	Oxygen	Air
	222	168	288	373	314

and that a single crystal behaves like an ordinary polycrystalline metal in the glow discharge when used as a cathode. They calculated the work-function of pyrite for electrons to be 4.8 volts.

In the **electrolysis** of pyrite suspended in molten potassium hydroxide, E. F. Smith noted that with a nickel crucible as cathode, and a platinum wire as anode, about half the sulphur is oxidized; with marcasite, oxidation is complete. R. Saxon observed that with finely-powdered pyrite in 10 per cent. sulphuric acid, with iron as cathode, carbon as anode, both ferrous and ferric sulphates appear in the electrolyte, and if an iron anode is used, only ferrous sulphate is formed. He also noticed that if pyrites be immersed in a soln. of ammonium sulphate and chloride, and subject to electrolysis whilst the pyrites is in contact with the carbon electrode, iron passes into soln. I. Bernfeld observed that with a pyrite anode in acidic soln., iron goes into soln., and with small current densities sulphur is deposited on the anode, and with large current densities, sulphuric acid is formed; with pyrite as anode in alkaline soln., iron is converted into hydroxide and all the sulphur forms sulphuric acid; with pyrite as cathode in acidic soln., hydrogen sulphide appears at the cathode; and with pyrite as cathode in alkaline soln., sulphur forms alkali sulphide. K. Fischbeck studied the cathodic reduction of pyrite in 2 per cent. sulphuric acid; M. Padoa and B. Zanella, the electrolysis of soln. of ammonium or sodium chloride and ammonium thiocyanate soln. with a pyrite anode, whereby the iron goes into soln. in the ferric state; and R. C. Wells, the anodic and cathodic polarization of pyrite in soln. of potassium chloride.

A. W. Smith<sup>15</sup> found that the **Hall effect** with pyrite increases proportionally with the magnetic field; and G. Nicolai gave for field of  $H$  gauss:

$H$	9,150	10,100	11,150	12,200	13,300	14,400
Hall constant	-21.7	-22.9	-28.0	-33.0	-38.0	-42.0

The **magnetic properties** of pyrite were examined by J. J. Berzelius,<sup>16</sup> T. J. Seebeck, M. Faraday, and C. B. Greiss. F. Gieseler said that the pure sulphide is non-magnetic. J. Huggett and G. Chaudron also said that pyrite is non-magnetic and that it undergoes oxidation at  $400^\circ$ . R. Juza and W. Biltz observed the susceptibility of different sulphides, and the results are summarized in Fig. 635, along with the results of observations on the X-radiograms. According to F. Stutzer and co-workers, the **magnetic susceptibility** of pyrite is  $4.53 \times 10^{-6}$  vol. unit; and L. C. Jackson said that the susceptibility is independent of the temp.; and after making allowance for the diamagnetic properties of the sulphur atoms in iron pyrites, the iron atom possesses a small, residual, positive magnetic moment. W. R. Crane gave

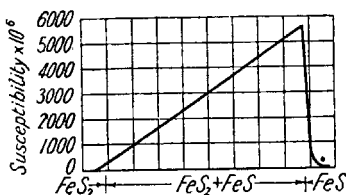


FIG. 635.—The Magnetic Susceptibility of the Iron Sulphides.

$1.860 \times 10^{-6}$  to  $159 \times 10^{-6}$  for the mass magnetic susceptibility of pyrite; and F. Stutzer and co-workers,  $4 \times 10^{-6}$ , for the coeff. of magnetization. The subject was studied by G. Grenet, and L. Pauling and M. L. Huggins.

**The physical properties of marcasite.**—The general mode of occurrence, and preparation of marcasite have been discussed in connection with pyrite; and there are, as in the case of pyrite, pseudomorphs after pyrrhotite, galena, copper pyrites, siderite, calcite, barytes, etc. The **colour** of marcasite is pale bronze-yellow, with a tinge of green; the colour deepens on exposure. The mineral readily tarnishes. The streak is greyish- or brownish-black. J. L. C. Schroeder van der Kolk<sup>17</sup> said that the streak is greenish-grey. J. A. Hedvall discussed the changes in colour which occur on heating the mineral. Marcasite occurs in stalactitic forms with a radiating internal structure, having the exterior sometimes covered with projecting crystals. The stalactitic form may occur in layers with galena or sphalerite, or both, and this resembles schalenblende, hence it has been called *Schalenmarcasite*. Marcasite also occurs in globular, reniform, and other imitative shapes. The general appearance of marcasite has given rise to some special descriptive terms. For example, *radiated pyrites*—*Strahlkies*—occurs in radiating masses and in simple crystals; *cockscomb pyrites*—*Kammkies*—occurs in aggregates of flattened, twinned crystals having crest-like forms; *spear pyrites*—*Speerkies*—occurs in twinned crystals with re-entering angles which have some resemblance to the head of a spear; *capillary pyrites*—*Zellkies*—occurs in cellular masses formed by the incrustation of crystals of other minerals that have disappeared, the marcasite is here usually mixed with pyrite; and *hepatic pyrites*—*Leberkies pyrites fuscus*—occurs massive in dull colours, and the term includes brown specimens of any pyrite altered more or less to limonite.

R. J. Haiiy, C. C. Leonhard, and J. A. H. Lucas showed that the **crystals** of marcasite, or *fer sulfure blanc*, are rhombic. J. J. Bernhardt, J. F. L. Hausmann, and F. Mohs also made observations on the rhombic crystals, although A. Gehmacher showed that some measurements agreed with the assumption that some crystals are monoclinic. The axial ratios of the rhombic crystals given by A. Sadebeck are:  $a : b : c = 0.7662 : 1 : 1.2342$ ; V. M. Goldschmidt gave  $0.7580 : 1 : 1.2122$ ; J. F. L. Hausmann,  $0.75241 : 1 : 1.18473$ ; G. T. Prior,  $0.7662 : 1 : 1.2342$ ; A. Gehmacher, and W. F. de Jong,  $0.762256 : 1 : 1.216698$ ; and for the artificial crystals, E. T. Allen and co-workers gave  $0.7646 : 1 : 1.2176$ . The common habit of the crystals of marcasite is pyramidal and also tabular, parallel to the (001)-face; with the brachydomes and pinacoids deeply striated parallel to the (010)/(001)-edge. E. T. Allen and co-workers found that the artificial mineral has these faces similarly striated, and the pyramid and prism zones are even more prominently striated parallel to the base; the common habit of the artificial crystals is also tabular, and pyramidal. The crystals of marcasite show **twinning** about the (110)-plane, and the twinning is frequently repeated so as to produce, in some cases, stellate fivelings; twinning about the (101)-plane is less frequent, and the crystals then cross at angles approaching  $60^\circ$ . The twinning was discussed by C. Viola, F. Wallerant, and F. Schöndorf and E. Schroeder. E. T. Allen found that the artificial crystals occur twinned about the (110)-plane, and that they are tabular parallel to this plane, and elongated along the vertical axis, and the (101)- and (011)-domes are prominent. The artificial pyramidal crystals are developed more symmetrically than the tabular crystals, and they are less frequently twinned. The (101)- and (011)-domes are characteristic, and the striated prisms, (110), are usually prominent. The crystals of marcasite were described by M. J. Buerger, G. Flink, F. A. Bannister, N. Watitsch, C. A. Tenne, O. Luedecke, C. O. Trechmann, F. Sandberger, E. R. Smith and R. A. Schroeder, W. D. Johnston, G. Werner, P. Groth, A. Breithaupt, A. Frenzel, A. Stelzner, H. Traube, E. Thomson, F. Roemer, B. Kosmann, C. Hintze, A. Gehmacher, V. R. von Zepharovich, A. Koch, A. Brunlechner, G. Grattarola, A. d'Achiardi, G. la Valle, P. Tschirwinsky, A. Lacroix, R. P. Greg and W. G. Lettsom, J. H. Collins, P. von Jereméeff,

J. D. Dana, etc. The **cleavage** on the (110)-face is rather distinct, while that on the (011)-face appears only in traces. The corrosion figures were studied by H. Schneiderhöhn; and the microscopic structure of polished surfaces also, by F. N. Guild, and H. Schneiderhöhn. J. Königsberger distinguished the anisotropy of marcasite from the isotropy of pyrite. W. F. de Jong found that **X-radio-grams** of marcasite correspond with a lattice with  $a=6.79$  Å.,  $b=4.45$  Å., and  $c=5.42$  Å.—the values for mispickel being  $a=6.44$  Å.,  $b=4.76$  Å., and  $c=5.63$  Å.

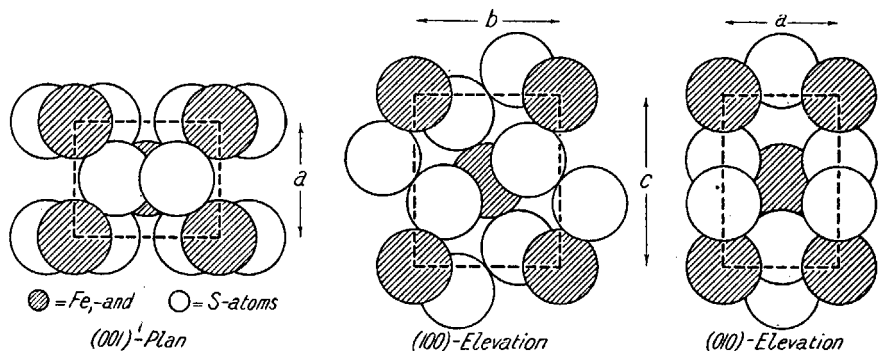


FIG. 636.—The Arrangement of the Atoms in Crystals of Marcasite.

M. J. Buerger found that there are two  $\text{FeS}_2$ -mols. per unit cell; and that the lattice dimensions are  $a=3.37$  Å.,  $b=4.44$  Å., and  $c=5.39$  Å. The paired sulphur atoms are 2.25 Å. apart; the unpaired sulphur atoms, 2.96 Å.; the iron atoms, 5.52 Å.; and the sulphur-iron atoms, 2.21 Å. The atoms in the (001)-, (100)-, and (010)-elevations are indicated in Fig. 636. N. Alsén observed the parameters:  $a=3.35$  Å.,  $b=4.40$  Å., and  $c=5.35$  Å., and his construction of the arrangement of the component atoms is indicated in Fig. 637. Observations were made by P. F. Kerr, by H. V. Anderson and K. G. Chesley, F. R. and K. R. van Horn, and by W. Jansen. M. L. Huggins discussed the structure of the space-lattice and assumed that the sulphur atoms occur in pairs, each sulphur atom being linked, by pairs of electrons, to one sulphur atom and four iron atoms, and each iron atom to six sulphur atoms.

C. F. Rammelsberg gave 4.865 to 4.900—best representative value 4.90—for the **specific gravity** of marcasite; V. Pöschl found 4.607 to 4.879; E. Madelung and R. Fuchs, 4.8487; H. N. Stokes, 4.880 to 4.891; F. Sandberger, 5.08; F. E. Neumann, 4.882; J. D. Dana, 4.678 to 4.847; A. Breithaupt, 4.601 to 4.879; G. Rose, 4.848; and C. Hintze, 4.65 to 4.88. F. Wöhler's value, 4.74, is too low. The best representative value is 4.88. E. T. Allen gave 4.887 at 25° for the sp. gr. of artificial marcasite, and found that when the compound is heated to 610° for some time the sp. gr. rises to 4.911, corresponding with its transformation to pyrite, whose sp. gr. is  $>5.02$ . The lower value observed is attributed to the porosity of the product. Other observations were made by C. Hatchett, A. P. Brown, G. Rose, E. Palla, A. A. Julien, N. Watitsch, E. T. Allen and co-workers, and E. Stutzer and co-workers. J. J. Saslawsky discussed the contraction which occurs when marcasite is formed from its elements. According to A. A. Julien, the **hardness** of marcasite on the macrodome face is 6, and on most of the other faces, 6.5. V. Pöschl found that for loads of 20 and 50 grms., the scratching hardness of marcasite is respectively 140.2 and 134.1 when the value for topaz, as

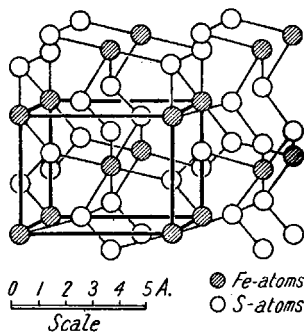


FIG. 637.—The Structure of Marcasite.

standard, is 1000; the corresponding values for pyrite are 182.2 and 199.1 respectively—*vide supra*, pyrite. O. Mügge observed no change in marcasite after it had been subjected to a press. of 20,000 atm. E. Madelung and R. Fuchs gave 0.0681 for the coeff. of **compressibility** in megabars per sq. cm.

The **specific heat** of marcasite may be a little greater than that of pyrite, though the available evidence is not sufficient to prove the statement. H. V. Regnault gave 0.1332 for the sp. ht. of marcasite, and A. Sella, 0.1460. As shown by E. T. Allen and co-workers, and E. Arbeiter, and indicated in connection with pyrite, marcasite slowly changes into pyrite by a monotropic or irreversible change; the speed of the reaction is accelerated by a rise of temp. and is attended by an evolution of heat—Fig. 638—and a decrease in the electrical resistance, but the

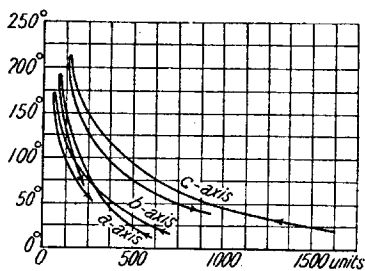


FIG. 638.—Action of Heat on the Electrical Conductivity of Marcasite.

change is not influenced by an increase of press. up to 10,000 atm.—*vide supra*, pyrrhotite, and pyrite. E. Arbeiter showed that when marcasite is heated in vacuo, sulphur is distilled off. R. Cusack gave 642° for the **melting-point** of marcasite, and J. Joly 440°, but since marcasite passes into pyrite below this temp., these statements do not mean what they say. A. Cavazzi found the **heats of combustion** of pyrite and marcasite are the same, namely, 1.55 Cals., but, as E. T. Allen and co-workers showed, the contained energy of marcasite is probably greater than that of pyrite (*q.v.*).

J. Königsberger gave 3.5 for the **refractive index** of marcasite calculated from the electrical conductivity. C. Doelter found that marcasite is opaque to the **X-rays**. O. Rohde found that marcasite has a larger **photoelectric effect** than pyrrhotite, but a smaller one than pyrite.

F. Beijerinck, and R. G. Harvey found that the **electrical conductivity** of marcasite is much smaller than that of pyrite (*q.v.*). The values for the electrical conductivity of marcasite, in Siemen's units, taken parallel to each of the three axes, are indicated in Fig. 638. K. Baedeker gave 16.56 ohms for the **electric resistance** at 0° and parallel to the *b*-axis; and A. Wesely, 2.4 ohms at 0°. Observations were made by T. du Moncel. According to J. Königsberger and O. Reichenheim, the conductivity of marcasite is 500 times smaller than that of pyrite. A crystal of marcasite which had been heated to 400°, had the electrical resistance, *R*, parallel to the *b*-axis, at  $\theta^\circ$ ,  $R = 16.58(1 + 0.00264\theta + 0.00009\theta^2) - 18500/(\theta + 273)273$ . The values taken parallel to the *a*- and *c*-axis are nearly the same. The observed values parallel to the *b*-axis are:

$\theta$	16°	65°	118°	150°	180°	220°	243°	-78°	-130°
<i>R</i>	10.25	4.68	2.75	2.20	1.81	1.50	1.30	242	>2600

The **thermoelectric force** of marcasite was studied by M. Kimura and co-workers, and T. du Moncel. R. C. Wells found the **electrode potential** of marcasite in *N*-KCl to be 0.72 volt; in *N*-H<sub>2</sub>SO<sub>4</sub>, 0.94 volt; in *N*-NaOH, -0.22 volt; and in *N*-Na<sub>2</sub>S, -0.07 volt. A. Lipschitz and R. von Hasslinger observed that the **electromotive force** of marcasite is positive against a calomel electrode in sulphuric acid with and without ferrous and ferric sulphates; and V. H. Gottschalk and H. A. Buehler, that marcasite in distilled water against copper gives 0.37 volt. E. F. Smith observed that the sulphur of marcasite is completely oxidized when a suspension of the powdered mineral in molten potassium hydroxide is electrolyzed under conditions where about half the sulphur of pyrite is oxidized. K. Fischbeck studied the electrochemical reduction of marcasite; M. Padoa and B. Zanella, the electrolysis of soln. of ammonium or sodium chloride, and ammonium thiocyanate whereby the iron dissolves in the ferric state; and R. C. Wells, the anodic and

cathodic polarization of marcasite. F. Stutzer and co-workers found the **magnetic susceptibility** of marcasite to be  $5.43 \times 10^{-6}$  vol. unit. J. Huggett and G. Chaudron said that marcasite is non-magnetic and it undergoes oxidation in air at  $400^{\circ}$ .

**A comparison of pyrite and marcasite.**—A general comparison of the properties of pyrite and marcasite—summarized by A. A. Julien <sup>18</sup> (with modifications) in Table XCIV—shows that the colour of pyrite is brass-yellow, that of marcasite is more grey. H. N. Stokes added that with suitable precautions against misleading tarnish colours, pyrite can be readily distinguished from marcasite by the colour, but it is sometimes impossible to draw any satisfactory conclusions from the colours of fine-grained concretions, or from specimens with rough surfaces. The crystals of pyrite are cubic; those of marcasite rhombic; the habit of pyrite is striated cubes or pentagonal dodecahedra, that of marcasite is tabular or pyramidal, usually fibrous and radiating. The fracture of pyrite is usually conchoidal, that of marcasite uneven and radiating. The streak of pyrite has usually a greenish tinge; that of marcasite, greyish. C. Frebold distinguished pyrite from marcasite by their X-radiograms. E. Grill treated both minerals with hydrogen peroxide, but pyrite alone gives a deposit of sulphur. The sp. gr. of pyrite is greater—representative values at  $25^{\circ}$  being 5.03 for pyrite and 4.88 for marcasite, but H. N. Stokes added that the attempt to calculate the proportions of marcasite and pyrite from the sp. gr. of the sample is illusive. Pyrite is slightly harder than marcasite; the electrical conductivity of pyrite is 500 times that of marcasite. Marcasite is more susceptible to atm. oxidation at ordinary temp. or when heated. Pyrite dissolves completely in nitric acid, whilst marcasite dissolves with the separation of sulphur.

L. Gedel, and R. Scheuer separated the different sulphides of iron by treatment with conc. hydrochloric acid. The powdered mixture is extracted with carbon disulphide to remove free sulphur; then treated with conc. acid whereby ferrous sulphide dissolves completely, whilst ferric sulphide dissolves with the separation of an equivalent of sulphur:  $\text{Fe}_2\text{S}_3 + 4\text{HCl} = 2\text{FeCl}_2 + 2\text{H}_2\text{S} + \text{S}$ . The sulphur is extracted by carbon disulphide, and calculated to ferric sulphide. The residual iron disulphide is dissolved by conc. nitric acid or aqua regia. The proportion of ferrous sulphide can be calculated from the total sulphur or total iron, and that present as  $\text{Fe}_2\text{S}_3$  and  $\text{FeS}_2$ . C. W. Dickson observed that whilst pyrrhotite is completely soluble in 10 per cent. nitric acid, magnetite is scarcely attacked.

According to H. N. Stokes, if the mineral is boiled with a soln. of iron-alum containing a gram of ferric iron, and 16 c.c. of 25 per cent. sulphuric acid per litre, the proportion of sulphur oxidized in the case of pyrite is 60.4 per cent. of the contained sulphur, whilst with marcasite only 18 per cent. is oxidized. The reaction was utilized by E. T. Allen and co-workers for finding the relative proportions of marcasite and pyrite in a sample of pyrites—*vide infra*. The chemical analysis of pyrites was described by E. T. Allen and J. Johnston, F. Chio, M. Ditrach, L. Gadais, E. Mengler, R. Müller, P. L. Robinson and co-workers, A. M. Smoot, G. Weyman, and E. Zintl and F. Schloffer.

**The chemical properties of pyrite and marcasite.**—H. Rose <sup>19</sup> observed that pyrite dissociates at a lower temp. when it is heated in hydrogen than when it is heated simply in a closed vessel. No hydrogen sulphide was formed. H. Conder, and T. J. Drakeley, however, found that at a dull red-heat, hydrogen sulphide and ferrous sulphide are formed; whilst G. Gallo said that three stages can be detected in the reduction: (i)  $2\text{FeS}_2 + \text{H}_2 = \text{Fe}_2\text{S}_3 + \text{H}_2\text{S}$ , commencing at  $228^{\circ}$  to  $230^{\circ}$ ; (ii)  $\text{Fe}_2\text{S}_3 + \text{H}_2 = 2\text{FeS} + \text{H}_2\text{S}$ , commencing at  $280^{\circ}$  to  $285^{\circ}$ ; and (iii)  $\text{FeS} + \text{H}_2 = \text{Fe} + \text{H}_2\text{S}$ , commencing at  $370^{\circ}$  to  $375^{\circ}$ . No sulphur compound analogous to  $\text{Fe}_3\text{O}_4$  was observed—*vide supra*, the preparation of ferrous sulphide. H. Conder discussed the “hydrogen roasting” of pyrites to recover sulphur and iron. When pyrite is heated in air, it furnishes sulphur dioxide, and ferrous sulphate, but at a higher temp., a basic ferric sulphate or ferric oxide is formed. Next to sulphur, pyrites is the most important material for the manufacture of



the sulphur dioxide required for the manufacture of sulphuric acid. For this purpose the pyrites is roasted in special ovens. If the pyrite be heated in a closed vessel with a limited supply of air, so that the pyrite is in excess, the products are sulphur dioxide and ferrous sulphate; and if the pyrite is heated in air to 100°, or ground dry in a mortar, these are the first products of the oxidation. P. Truchot represented the reactions involved in roasting pyrites by the equations:  $\text{FeS}_2 + \text{O}_2 = \text{FeS} + \text{SO}_2$ ;  $2\text{FeS} + 3\text{O}_2 = 2\text{FeO} + 2\text{SO}_2$ ;  $2\text{FeO} + \text{O} = \text{Fe}_2\text{O}_3$ ;  $2\text{SO}_2 + \text{O}_2 = 2\text{SO}_3$ , and  $2\text{FeO} + 2\text{SO}_3 = 2\text{FeSO}_4$ , and at about 530°,  $2\text{FeSO}_4 = \text{SO}_2 + \text{SO}_3 + \text{Fe}_2\text{O}_3$ . In some cases, ferrosic oxide is formed:  $\text{FeS}_2 + 10\text{Fe}_2\text{O}_3 + \text{O}_2 = 7\text{Fe}_3\text{O}_4 + 2\text{SO}_2$ .

TABLE XCIV.—COMPARISON OF PYRRHOTITE, MARCASITE, AND PYRITE.

	Pyrrhotite	Marcasite	Pyrite
Composition.	$\text{Fe}_8\text{S}_8$ to $\text{Fe}_{16}\text{S}_{17}$ , and commonly nickeliferous	$\text{FeS}_2$	$\text{FeS}_2$
Hardness with steel	3.5-4.5	6.0-6.5 Striking fire imperfectly, with strong sulphurous odour	6.0-7.0 Striking fire readily with weak sulphurous odour
Specific gravity	4.4-4.68 (4.67)	4.68-4.85 (4.88)	4.74-5.19 (5.03)
Colour.	Bronze - yellow to steel to black-brown	Greyish-white to bronze-yellow	Golden to pale brass-yellow
Streak.	Greyish-black	Greenish - grey to brownish-black	Brownish-black
Fracture	Uneven	Uneven, radiating	Conchoidal to uneven
Grains.	Compact and magnetic	Columnar structure	Often fibrous and radial
Crystals	Rare: hexagonal, generally tabular, and magnetic	Common: Orthorhombic, often in striated twins, toothlike or crested forms, etc.	Abundant: isometric cubes, pyritohedra, octahedra, etc.
Ignition in closed tube	Unchanged	Yielding a sublimate of sulphur and a magnetic residue	(Like marcasite)
Heating to 450°	Stable	Stable	Converted to pyrite
Specific heat	0.1500	0.1332	0.1306
Nitric acid	Insoluble	Soluble with separation of sulphur	(Like marcasite)
Hydrochloric acid.	Soluble with separation of sulphur and hydrogen sulphide	Insoluble	Insoluble
Alteration	Iridescent tarnish	Iridescent, often efflorescent	Iridescent, efflorescent, or hepatic colour.

The formation of soluble sulphate after 6 hrs'. roasting amounted to 1.0108; after 12 hrs', 0.4816; and after 18 hrs', 0.0994 per cent. This shows that the sulphate is formed early in the operation of roasting pyrite, and decomposes in the later stages. If the supply of air is very limited, and if the temp. is high enough, some sulphur may distil off as well—*vide supra*, the action of heat on pyrite—and in large pieces, sulphur may distil from the interior and burn at the surface. In either case pyrrhotite is formed to which A. Scheurer-Kestner and A. Rosenstiehl gave the formula  $\text{FeS}$ ; T. Sidot,  $\text{Fe}_3\text{S}_4$ ; and H. V. Regnault,  $\text{Fe}_5\text{S}_6$ —*vide supra*. If the temp. rises rapidly, the ferrous sulphide may fuse before the volatiles are evolved, and leave a vitreous, vesicular slag. The air which has access to the surface of the pyrite forms a film of ferric oxide, which, according to A. Lemoine, oxidizes the ferrous sulphide lower down, and the reduced ferric oxide is re-oxidized by the air.

The reaction was studied by T. L. Phipson, T. Gibb, F. Warlimont, F. Bode, E. Richters, E. Knop, M. Fortmann, B. G. Bredberg, J. L. Proust, M. Bräuning, F. C. Thompson and N. Tilling, J. Milbauer and J. Tucek, W. Eitel, H. Saito, B. Neumann and co-workers, J. Jelinek, H. W. Nelson and co-workers, H. E. Woisen, and I. N. Kuzminukh. P. Truchot gave  $440^{\circ}$  to  $450^{\circ}$  for the temp. at which the oxidation of the sulphur in pyrite begins; A. W. Warwick said  $290^{\circ}$ – $315^{\circ}$ , and the heat of the oxidation may raise the temp. to  $455^{\circ}$ . J. W. Mellor compared the percentage amounts of the contained sulphur in pyrite and marcasite after heating 2 to 3 hrs. at different temp. in a current of air, and the results are summarized in Fig. 639. They show that the oxidation of marcasite sets in before that of pyrite, but thereafter they follow along similar lines. The subject was studied by F. G. Jackson. A. W. Warwick measured the result on a rising temp. and found that a sample with 15.2 per cent. of sulphur, after heating :

Time . . . . .	0	1	2	3	4	8	18 hrs.
Temperature . .	$150^{\circ}$	$203^{\circ}$	$203^{\circ}$	$203^{\circ}$	$321^{\circ}$	$357^{\circ}$	$400^{\circ}$
Sulphur . . . .	15.2	13.2	10.1	7.4	5.6	2.1	0.11 per cent.

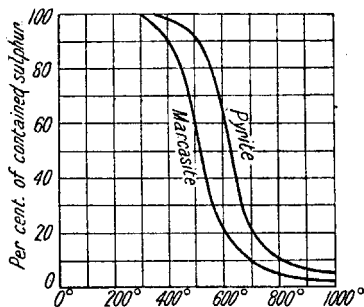


FIG. 639.—The Oxidation of Pyrite and Marcasite at Different Temperatures in Air.

There was no evidence of the formation of an intermediate ferrous sulphide, and he represented the reaction by the equations:  $\text{FeS}_2 + 5\text{O} = \text{FeO} + 2\text{SO}_2$ ;  $2\text{SO}_2 + \text{O}_2 = 2\text{SO}_3$ ;  $\text{SO}_3 + \text{FeO} = \text{FeSO}_4$ ;  $\text{FeSO}_4 + \text{FeO} = \text{Fe}_2\text{O}_3 + \text{SO}_2$ ; the initial and end states being  $4\text{FeS}_2 + 11\text{O}_2 = 2\text{Fe}_2\text{O}_3 + 8\text{SO}_2$ . The roasting of pyrites—pyrite and marcasite—for sulphur dioxide (*q.v.*) has played an important part in the manufacture of sulphuric acid. A. Wurm showed that in some cases sulphur may be formed by the oxidation:  $\text{FeS}_2 + 7\text{O} + \text{H}_2\text{O} = \text{FeSO}_4 + \text{H}_2\text{SO}_4$ ;  $6\text{FeSO}_4 + 3\text{O} + 3\text{H}_2\text{O} = 2\text{Fe}_2(\text{SO}_4)_3 + 2\text{Fe}(\text{OH})_3$ ;  $\text{FeS}_2 + \text{H}_2\text{SO}_4 = \text{FeSO}_4 + \text{H}_2\text{S} + \text{S}$ ; and  $\text{FeS}_2 + \text{Fe}_2(\text{SO}_4)_3 = 3\text{FeSO}_4 + 2\text{S}$ . The formation of sulphur in the weathering of pyrites was discussed by E. Dittler. The sparks obtained when pyrites is struck with steel, were attributed by A. Johnsen to the heat developed by the friction oxidizing the particles and the heat so developed raised them to a red-heat. G. F. Hüttig and P. Lürmann showed that the reaction between pyrites and oxygen is reversible, that the final product is a solid soln. of oxide and sulphide; and that these two react on cooling to form ferrous sulphate:  $4\text{Fe}_2\text{O}_3 + \text{FeS} = \text{FeSO}_4 + 8\text{FeO}$ . The composition of the solid soln. is given by  $n^{-1} = 13.0 - 6.66 \log(p_{\text{SO}_2}/p_{\text{O}_2})$ , where  $n^{-1}$  is the Fe:S ratio. E. F. Smith discussed the electrolytic oxidation of pyrites in molten alkali hydroxide—*vide supra*.

According to J. J. Berzelius, many samples of pyrites are converted into hydrated ferric oxide and sulphuric acid when exposed to moist air, and marcasite, indeed, often becomes quickly covered with an efflorescence of ferrous sulphate. J. J. Berzelius thought that the fact that the efflorescence shows itself only irregularly on a mass of marcasite, shows that ferrous sulphide is present as well as iron disulphide. The two form a galvanic couple with the disulphide forming the negative pole. The disulphide, he added, remains unaltered, but is shattered by the expansive force of the growing crystals of ferrous sulphate. When the soluble salt is washed out by water, there is no evidence of the formation of free sulphur. L. Gmelin reported free sulphur in the products of the efflorescence of marcasite from Schriesheim. J. J. Berzelius found a sample which effloresced in humid air in 12 hrs., expanded ten-fold in 4 days. Iron pyrites imperfectly roasted

so that only a part of the disulphide is converted to monosulphide, shows a marked tendency to efflorescence.

Many examples have been quoted—by J. S. Newberry, J. Gray, A. de Selle, P. A. Dufrenoy, G. F. Becker, T. Egleston, T. Scheerer, A. Girard and H. Morin, and C. Méne—but explanations are not so easy to find. J. F. Henckel attributed the ready weathering to the presence of impurities, density, texture, etc., as he said *unius rei plures possunt esse causæ*; A. G. Werner also suspected that the presence of arsenic might favour decomposition; J. J. Berzelius, manganese, etc.; F. Stromeyer, free sulphur; and C. Hatchett, the presence of “a small portion of oxygen being previously combined with a part, or with the general mass of sulphur, at the time of the original formation of these substances, so that the state of the sulphur is tending to that of oxide, and thus a further addition of oxygen becomes facilitated.” J. L. Proust considered that pyrites with the smallest proportion of sulphur are most liable to decomposition, but C. Hatchett said that this is so far from being in accord with facts, that “I might be induced to adopt the contrary opinion.” J. J. Berzelius considered that the presence of pyrrhotite in pyrites favoured the weathering of pyrites, but F. Köhler considered that his analyses did not agree. Later on, J. J. Berzelius said that it seems “highly probable that the falling asunder of ordinary pyrites arises from the electrochemical action of electronegative bisulphuret which is here and there mixed with it in small particles.” F. Senft favoured this hypothesis. A. Girard and H. Morin attributed the phenomenon to “the enclosure of a clay easily attacked either by atmospheric agents, or by water, may well be a ready cause of their alteration.” J. Fournet said that “a spontaneous tendency to dimorphism produces the disintegration of the minerals, and this is followed by chemical action.” He asked: May not prismatic marcasite be simply an unstable form of pyrites, pyrite, the stable form? just as prismatic aragonite is the unstable form of calcium carbonate, and rhombohedral calcite the stable form. J. Nicol, and J. P. Kimball attributed the difference in the tendency to decomposition on exposure to the atmosphere, to some peculiarity in the state of molecular aggregation, or to molecular differences arising from crystalline structure. A. A. Julien found that the varieties of pyrites which weather easiest are mixtures of marcasite and pyrite in intimate association. H. Schneiderhöhn attributed the differences to the presence of colloidal disulphide which is very susceptible to attack; and F. Zirkel found pyrite from sedimentary deposits weathers more readily than that from crystallized rocks. The subject was discussed by H. Willert. According to U. Panichi, if the (111)-faces of pyrite predominate, the crystals succumb to attack far more readily than if the (210)-faces are dominant. F. Katzer attributed the resistance of a pyrite from Bornia to the compact nature of the surfaces of the crystals. F. Carmichael observed that powdered marcasite agitated for 13 days with water and oxygen, suffers 0.29 per cent. oxidation, and pyrite, 0.02 per cent.

J. J. Berzelius added that since the efflorescence of pyrites is attended by the evolution of heat, the spontaneous inflammation of pyritiferous coals may be explained when the coals are heaped up in masses—within or without the mine—and exposed to humid air. H. Macpherson and co-workers showed that not only is the heat of oxidation of importance, but that the disintegration produced by the volume changes on oxidation, noted by J. J. Berzelius, facilitates the access of air to the coal itself, and that this favours rapid oxidation and ignition. The drainage water from some mines contains ferrous sulphate derived from the oxidation of pyrites. Advantage is taken of the reaction in the old method of preparing ferrous sulphate by exposing pyrites in heaps in moist air, and collecting the drainage water in tanks for evaporation. The manufacture of fuming sulphuric acid (*q.v.*) near Nordhausen involves the oxidation of the pyritiferous slates to form the vitriol stone—a mixture of ferrous and ferric sulphates—which is subjected to dry distillation for the acid. W. H. Emmons said that the heat of oxidation is enough to raise the temp. of average mine-water by 12.7°.

E. F. Smith found that a current which would completely oxidize the sulphur in marcasite in a given time would oxidize less than half of the sulphur in pyrite in the same time. This remaining sulphur was held very tenaciously, though the mineral was subjected to more powerful currents and longer-continued action than in the case of marcasite or pyrrhotite. Finally, by adding an equal quantity of cupric oxide, and using a more powerful current, all of the contained sulphur was oxidized. Previous to the addition of cupric oxide but 21 or 22 per cent. of the sulphur was oxidized.

The first sign of weathering is the dulling of the surface which then becomes matt, and later brown. When the grains of pyrites have succumbed to weathering influences, there is a brownish film of limonite or goethite admixed with a little yellowish-green free sulphur, and ferric and ferrous sulphates. This subject was discussed by W. Mietzschke, M. Rolland, F. von Kobell, F. Senft, O. J. Heinrich, H. Bauerman, J. Roth, J. R. Blum, and G. Rose. S. H. Emmens represented the order in which sulphides oxidize, beginning with the one most easily attacked: marcasite, millerite, chalcocite, galena, and zinc blende; C. R. van Hise gave: Fe, Cu, Zn, Pb, and Ag sulphides; W. H. Emmons gave: sphalerite, chalcocite, pyrrhotite, chalcopyrite, pyrite, galena, and enargite; whilst for the attack with 0.057*N*-H<sub>2</sub>SO<sub>4</sub>, R. C. Wells gave: pyrrhotite, sphalerite, galena, chalcopyrite, and pyrite; and V. H. Gottschalk and H. A. Buehler measured the e.m.f. of various mineral sulphides in distilled water against copper—*vide supra*. F. Köhler showed that the crust on weathered marcasite may contain a comparatively large proportion of ferrous sulphate, and this crystallizing in the minute pores and fissures forms an efflorescence, and, as indicated above, disintegrates the grains more completely. E. Arbeiter, and H. N. Stokes, in agreement with general observations, have shown that marcasite weathers much more rapidly than pyrite, and that some specimens of pyrite are remarkably resistant to weathering influences. The formation of basic sulphates, sulphates, and sulphuric acid in the early stages of the oxidation of pyrites, and the simultaneous formation of ferrous sulphide was discussed by L. Benedek, W. A. Caldecott, S. H. Emmens, J. Loczka, T. Scheerer, and C. Winkler. E. Dittler observed no sulphate formation in a current of carbon dioxide. T. F. Winmill observed no formation of ferric sulphate. E. T. Allen and co-workers found that in a sealed tube, filled with air, ferrous and ferric sulphates and sulphur dioxide are formed at 100°; a similar reaction occurs if pyrites is triturated in air, and in ordinary air at 75°, some hydroxide is formed. The stages in the transformation of pyrites to limonite are:  $\text{FeS}_2 \rightarrow \text{FeSO}_4 \rightarrow \text{Fe}_2(\text{SO}_4)_3 \rightarrow \text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ . The reactions have been symbolized:  $2\text{FeS}_2 + 7\text{O}_2 + 2\text{H}_2\text{O} = 2\text{FeSO}_4 + 2\text{H}_2\text{SO}_4$ ;  $12\text{FeSO}_4 + 3\text{O}_2 + 6\text{H}_2\text{O} = 4\text{Fe}_2(\text{SO}_4)_3 + 4\text{Fe}(\text{OH})_3$ . The ferrous and ferric sulphates may be in part washed away by currents of water, and if calcium, magnesium, barium, or strontium compounds are in the track of the underground current of water, crystals of sulphates of these bases may be formed—*e.g.*, epsomite, selenite, barytes, etc. J. W. Evans discussed this subject and represented the reaction with calcium carbonate:  $4\text{FeS}_2 + 15\text{O}_2 + 3\text{H}_2\text{O} + 8\text{CaCO}_3 = 2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O} + 8\text{CaSO}_4 + 8\text{CO}_2$ . The ferric sulphate in these waters is an active oxidizing agent, and acts as an oxygen carrier to surrounding ores. It acts on pyrite:  $\text{Fe}_2(\text{SO}_4)_3 + \text{FeS}_2 = 3\text{FeSO}_4 + 2\text{S}$ , and the nascent sulphur is oxidized to sulphurous and finally sulphuric acid. This subject was discussed by H. Schneiderhöhn, and F. C. Thompson and N. Tilling. The limonite may appear as a residual deposit like beds of laterite; as a so-called gossan-cap or a mass of porous limonite extending to a considerable depth in an outcrop of pyrite or chalcopyrite; and as pseudomorphs of limonite after pyrite. H. M. Chance, and S. H. Emmens discussed the pyritic origin of iron ores; G. M. Schwartz, and W. A. Tarr, the weathering of pyritic ores to limonite. H. Laubmann, P. W. Jeremejeff, E. Hussak, A. Lacroix, E. Geinitz, E. Döll, H. B. North, and J. R. Blum observed pseudomorphs of limonite after pyrite, or marcasite; J. R. Blum, goethite; G. C. Hoffmann, and J. R. Blum, hæmatite; A. Reuss, galena; J. Holdsworth, quartz; F. P. Mennel, bornite; H. A. Miers,

chalcocite ; F. Kretschmer, stilpnomelane ; and W. Eitel, R. Brauns, and O. Mügge, pyrrhotite. S. Hilpert said that the oxidation may go to ferrosic oxide ; and A. Lacroix to melanterite,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , if the oxidation has been rapid. A. R. Whitman represented the sequence in the formation of china-clay and chlorite from felspar by metasomatic replacement by the equations : (i)  $2\text{FeS}_2 + 2\text{H}_2\text{O} + 7\text{O}_2 = 2\text{Fe}(\text{HSO}_4)_2$  ; (ii)  $15\text{Fe}(\text{HSO}_4)_2 + \text{FeS}_2 = 2\text{FeS}_2 + 7\text{Fe}_2(\text{SO}_4)_3 + 7\text{H}_2\text{SO}_4 + 8\text{H}_2\text{O}$  ; (iii)  $4\text{KAlSi}_3\text{O}_8 + 3\text{H}_2\text{SO}_4 + 7\text{H}_2\text{O} = \text{H}_4\text{Al}_2\text{Si}_2\text{O}_9 + \text{Al}_2(\text{SO}_4)_3 + 2\text{K}_2\text{SiO}_3 + 8\text{H}_2\text{SiO}_3$  ; and (iv)  $\text{H}_4\text{Al}_2\text{Si}_2\text{O}_9 + 3\text{H}_2\text{SO}_4 = \text{Al}_2(\text{SO}_4)_3 + 2\text{H}_2\text{SiO}_3 + 3\text{H}_2\text{O}$ . According to A. Matsubara, natural sulphide ores convert the  $\text{H}^+$ -ions of ground water into  $\text{HS}^-$ -ions with a lower surface potential.

O. Weigel<sup>20</sup> observed that **water** dissolves 0.044889 mol of pyrite per litre, and 0.044084 mol of artificial pyrite ; E. Dittler found the solubility of pyrite in water is small, but increases if oxygen is passed through the liquid ; C. Doelter observed that at 80°, 0.10 grm. of pyrite dissolves in 100 grms. of distilled water ; and 0.037 grm. of marcasite dissolves in 100 grms. of water. Observations were also made by J. W. Evans, and E. Dittler. A. N. Winchell noted that by passing air through water with 300 grms. of finely-powdered pyrite in suspension for 10 months, an appreciable quantity of ferric sulphate and sulphuric acid passed into soln. F. F. Grout obtained similar results ; and V. A. Gottschalk and H. A. Buehler observed a more rapid attack. J. W. Gruner found that when 15 grms. of pyrite were treated with about 500 c.c. of peat water for 77 days, 23 parts of Fe per million passed into soln. ; and a trace only dissolved in 30 days. J. W. Evans showed that with frequently-renewed water, powdered pyrite is slowly decomposed forming soluble iron sulphate ; and that aerated water charged with calcium carbonate slowly converts pyrite into limonite as indicated above. C. A. Burghardt found that water in a sealed tube at 120° decomposes pyrite forming sulphuric acid, ferrous and ferric sulphates, and hydrogen sulphide. C. F. Tolman and J. D. Clark observed that when pyrite is kept with water in a sealed tube at 41° for 3 months, some hydrogen sulphide is formed. S. F. Emmons observed that water with dissolved hydrogen sulphide or alkali sulphide dissolves some pyrite ; and G. F. Becker found that at room temp., one part of pyrite is soluble in 1800 parts of 1.5 molar sulphide soln. H. Freundlich and co-workers studied the adsorption of water. H. Freeman also observed the solubility of iron sulphide in soln. of alkali sulphide. F. Foreman observed that in a sealed tube artificial pyrite in contact with water at 100° dissolved 0.64 part of Fe per million, and at 250°, 0.72 part per million. With natural pyrite :

SOLVENT	DISSOLVED	100°	150°	250°	320°		
Water	Fe	0.11	0.07	0.04	0.24	parts per million	
	Fe eq. $\text{H}_2\text{S}$	0.00	0.00	19.8	51.5	"	"
0.1N- $\text{NaHCO}_3$	Fe	0.02	0.04	0.07	0.24	"	"
	Fe eq. $\text{H}_2\text{S}$	0.00	10.05	19.50	—	"	"
0.1N- $\text{Na}_2\text{S}$	Fe	0.00	0.00	0.00	0.04	"	"
	Fe eq. $\text{H}_2\text{S}$	—	—	8.65	—	"	"

H. N. Stokes observed that by circulating alkaline water about pyrite and marcasite, hæmatite and hydrated ferric oxide are formed, and the sulphur forms alkali sulphide and thiosulphate. C. A. Burghardt observed that powdered pyrite and water in a sealed tube at 120° form hydrogen sulphide, sulphuric acid, ferric and ferrous sulphates, and a little hydrated ferric oxide. L. Benedek found that steam at 300° to 400° converts pyrite into ferrous oxide and hydrogen sulphide. E. T. Allen and co-workers added that pyrrhotite is an intermediate state in the reaction. E. Grünert represented the action of steam on pyrite by the equations :  $\text{FeS}_2 \rightleftharpoons \text{FeS} + \text{S}$  ;  $6\text{S} + 4\text{H}_2\text{O} \rightleftharpoons 4\text{H}_2\text{S} + 2\text{SO}_2$  ;  $\text{SO}_3'' + \text{S} = \text{S}_2\text{O}_3''$  ;  $\text{FeS} + \text{H}_2\text{O} = \text{H}_2\text{S} + \text{FeO}$  ; and  $3\text{FeO} + \text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + \text{H}_2$ . V. H. Gottschalk and H. A. Buehler discussed the relative speeds of oxidation of pyrite and marcasite under these conditions.

The reaction was studied by F. C. Thompson and N. Tilling. A. F. Taggart made experiments on the flotation of pyrite; E. Arbeiter found that **hydrogen dioxide** in 10 per cent. soln. with a little hydrochloric acid acts on powdered pyrite more readily than on marcasite. P. Ozeoff observed that both minerals are completely decomposed by 30 per cent. hydrogen dioxide; and E. Grill observed that with pyrite alone is there a separation of sulphur.

H. Moissan observed that **fluorine** does not attack pyrite in the cold, but at about 200° there is a violent attack. L. E. Rivot and co-workers found that when treated with alkali-lye through which **chlorine** is rapidly passed, finely-divided pyrite is completely decomposed. W. Kangro and R. Flügge found that at 900° all the iron was removed from pyrite in 30 minutes, and the distillate contained ferric chloride and sulphur monochloride. A. A. Julien found that **bromine** vapour at ordinary temp. attacks pyrite less rapidly than marcasite; and that the attack with bromine water is fairly rapid. J. Lemberg observed that a soln. of bromine in alkali-lye gradually decomposes pyrite. W. S. Allen and H. B. Bishop opened up the powdered mineral for analysis by shaking it with a soln. of bromine in carbon tetrachloride. H. Wurtz observed that, unlike pyrrhotite, pyrite is not dissolved by a freshly-prepared soln. of iodine, and E. Wilke-Dörfurt and E. A. Wolf found that pyrite is decomposed by heating it in the vapour of **iodine trichloride**. G. Gore, and E. Zalinsky observed that pyrite is insoluble in **hydrofluoric acid**. According to A. P. Brown, when dried **hydrogen chloride** is passed over pyrite and marcasite for an hour at 210°, the result is not very marked, but by raising the temp., the differences in the rates of attack on the two minerals is more marked. The percentage amounts of sulphur lost in the different cases were:

	15°	310°	325°	Red-heat
Pyrite . . . . .	0.93-0.94	10.73	17.13	46.47
Marcasite . . . . .	0.59-0.77	7.19	10.70	—

Pyrite is not easily attacked by dil. **hydrochloric acid**. A. P. Brown said that the cold or hot, conc. or dil. hydrochloric acid attacks the mineral very slowly; when pyrite was treated for an hour with the boiling conc. acid, of sp. gr. 1.2, only 2.56 out of 46.67 per cent. of iron passed into soln. Similar results were obtained with marcasite, and in both cases no evolution of hydrogen sulphide was observed. E. T. Allen and co-workers, and E. Weinschenk said that pyrite and marcasite are almost insoluble in hot, conc. hydrochloric acid, but V. Rodt observed that in the presence of strong reducing agents, like stannous chloride, pyrite, and particularly marcasite, are dissolved by the warm acid. H. St. C. Deville found that pyrite is converted by **hypochlorous acid** into iron sulphate. G. Spezia observed that an aq. soln. of **potassium chlorate**, at 15° to 16° for 21 hrs., oxidized some pyrite to sulphate.

E. E. and I. W. Wark studied the effect of sulpho-compounds on the flotation of pyrite. E. F. Smith found that pyrite and marcasite are not dissolved by cold **sulphur monochloride**, but at 140°, decomposition is complete, and ferric chloride is formed; H. B. North and C. B. Conover found that the reaction is complete in a sealed tube at 319°. H. Danneel and F. Schlottmann noted that the sulphide is attacked by **sulphuryl chloride**. According to A. Terreil, a 10 per cent. soln. of **alkali sulphide** attacks marcasite slowly, but not pyrite—*vide supra*. G. E. Becker also found that pyrite is far less readily attacked than marcasite by a soln. of sodium sulphide, or of hydrosulphide. C. Doelter observed that marcasite is more readily dissolved than pyrite by a soln. of sodium sulphide. The attack is favoured by raising the temp. The actions of sodium sulphide and hydrosulphide were studied by R. E. Stevens; pyrrhotite is formed. A. M. Gaudin and W. D. Wilkinson studied the action of dioxanthogens. R. F. Bacon treated iron sulphides with **sulphur dioxide** so as to liberate sulphur and produce iron oxide. L. Wöhler and co-workers, and the Rhenania Verein Chemischer Fabriken represented the reaction:  $3\text{FeS}_2 + 2\text{SO}_2 = \text{Fe}_3\text{O}_4 + 8\text{S}$ . J. Milbauer and J. Tucek observed

that ferrous sulphate is formed as an intermediate product particularly about 600°. The action of **sodium sulphite** was studied by R. E. Stevens, and represented by the equation:  $\text{FeS}_2 + \text{Na}_2\text{SO}_3 = \text{Na}_2\text{S}_2\text{O}_3 + \text{FeS}$ . Pyrites is but slowly affected by treatment with dil. **sulphuric acid**, and A. P. Brown, E. T. Allen and co-workers, and E. Divers and T. Shimidzu found that boiling, conc. sulphuric acid slowly decomposes both minerals with the evolution of sulphur dioxide, the formation of ferric sulphate, and the separation of sulphur. With pyrite during 1 hr's. action, 14·81 per cent. of iron dissolved, and with marcasite, 12·77 per cent. R. C. Wells found that the sulphides are attacked by 0·057*N*- $\text{H}_2\text{SO}_4$  in the order: pyrrhotite, sphalerite, galena, chalcopyrite, and pyrite. V. Lenher found that **selenium oxydichloride** attacks pyrite slowly in the cold, and vigorously when heated forming sulphur dioxide, and selenium monochloride.

A. P. Brown found that powdered pyrite gave no appreciable loss when heated to 325° in an atm. of **nitrogen**; and that when the powdered mineral is heated at 335°, in the vapour of **ammonium chloride**, a sublimate of ammonium sulphide is formed, and the amounts of sulphur lost by pyrite and marcasite in about 25 minutes, were respectively 7·06, and 9·50 per cent. Pyrite and marcasite are attacked by **nitric acid**, and by **aqua regia**, yielding a ferric salt, sulphuric acid, and sulphur. The reaction with nitric acid was studied by E. T. Allen and co-workers. H. B. Yardley observed that the sulphur is oxidized to sulphuric acid, and this more rapidly at 100° than at a higher temp. G. Kingsley found that with 5 per cent. nitric acid, no sulphate is formed at 75°, but only nitrate and sulphur. According to G. J. Brush and S. L. Penfield, when the finely-powdered minerals are treated with conc. nitric acid under the same conditions, pyrite dissolves completely, whilst marcasite leaves a residue of sulphur. A common method of opening pyrites for analysis, is to digest it with boiling aqua regia made by mixing 1 part of fuming hydrochloric acid with 3 or 4 parts of nitric acid of sp. gr. 1·36 to 1·40. According to G. Chaudron and G. Juge-Boirard, during the dissolution of pyrites in nitric acid or aqua regia, there is always a separation of free sulphur, in the case of marcasite or pyrites containing other sulphides, if the temp. exceeds 60°. If the acid is allowed to act at room temp., there is no separation of sulphur, but the time required for the dissolution is much longer. H. Rose observed that when pyrites is heated in **phosphine**, the reaction can be symbolized:  $3\text{FeS}_2 + 4\text{PH}_3 = \text{Fe}_3\text{P}_4 + 6\text{H}_2\text{S}$ . R. F. Weinland and L. Storz found that when powdered pyrite is heated many days with a soln. of **sodium arsenite**, some sulphur is formed—the reaction proceeds farther with marcasite. According to G. W. Plummer, when pyrites is heated to 250° with **arsenic trichloride** in a sealed tube, a colloidal soln. of arsenic, not arsenic sulphide, is formed; and when heated with an excess of **bismuth trichloride** in an atm. of carbon dioxide, decomposition is complete in about 5 minutes, and with both pyrite and marcasite, all the iron is in the ferrous state; the sulphur forms some monochloride, and about 91 per cent. appears as bismuth sulphide.

According to H. Rose, when pyrites is heated with **carbon**, carbon disulphide is formed; but A. Murlot, and T. J. Drakeley observed that at 500°, in an atm. of carbon dioxide, the sulphur is given off as hydrogen sulphide. According to E. Grünert, the reaction in an atm. of steam furnishes the phases which appear in the reactions between steam and pyrite, and between steam and carbon. The hydrolytic action on sulphur results in the formation of sulphur dioxide, which is reduced by the carbon. The desulphurization of the pyrites by carbon proceeds better in the presence of steam than in dry nitrogen, in the latter case, some sulphur is probably adsorbed by the carbon. F. C. Thompson and N. Tilling represented the reaction with **carbon monoxide** by  $\text{FeS}_2 + \text{CO} = \text{FeS} + \text{COS}$ . W. Thörner represented the reaction with **carbon dioxide** by the equation:  $\text{FeS}_2 + 2\text{CO}_2 + 2\text{H}_2\text{O} = \text{S} + \text{H}_2\text{S} + \text{Fe}(\text{HCO}_3)_2$ . The reaction was studied by F. C. Thompson and N. Tilling, and N. D. Costeanu. T. J. Drakeley, and L. Benedek found that dry carbon dioxide does not act at 500°, but the moist gas results in the formation of hydrogen sulphide; N. D. Costeanu observed that at 1000°, the pyrite decomposes

into ferrous sulphide and sulphur, and that the ferrous sulphide reacts with the carbon dioxide to produce carbon monoxide, sulphur, and ferrous oxide; at  $1100^{\circ}$ , ferric oxide takes the place of ferrous oxide. G. W. Plummer, and K. B. Rogers found that pyrites is readily decomposed when it is heated to  $250^{\circ}$  in the vapour of carbon tetrachloride. M. Berthelot said that **ether** in the presence of air extracts some sulphur from pyrites. According to H. C. Bolton, "three specimens of pyrite, with **citric acid** for 12 hrs. in the cold, gave no traces of gas, and three of pyrrhotite liberated it in the cold, and freely on boiling. All the specimens were decomposed by dil. hydrochloric acid excepting one sample of pyrite." By the prolonged contact of pyrite with a conc. soln. of citric acid, at  $15^{\circ}$  to  $22^{\circ}$ , there was evidence of decomposition in 8 days, and in a month, the soln. had acquired a reddish colour, and reacted for iron and sulphuric acid. Finely-powdered pyrite is quickly attacked by a mixture of potassium nitrate and citric acid in the cold, or by a boiling mixture of potassium nitrate or chlorate and citric acid. Parallel results were obtained with **tartaric acid** and potassium chlorate; and with **oxalic acid** and potassium nitrate. T. G. Pearson and P. L. Robinson found that, unlike ferrous and ferric sulphides, pyrite and marcasite are insoluble in soln. of **potassium cyanide**. E. Alberts studied the decomposition of pyrite when heated in the vapour of **carbon tetrachloride**. A. J. Scarlett and co-workers studied the emulsification of **benzene** by pyrites.

J. Struever observed that when pyrite is laid on **copper** foil, the metal is slowly blackened, and rapidly so with marcasite; similar results were obtained with **silver**. H. Ditz observed that a mixture of **aluminium** and pyrite furnishes 50 per cent. of the iron as metal when treated as in the thermite process; the remaining iron forms a slag of  $\text{Al}_2\text{S}_3 \cdot \text{FeS}$ .

J. A. Smythe found that when pyrite is treated with molten **potassium hydroxide**, at  $150^{\circ}$ , an intense blood-red colour is developed, which, when a little water is added, changes to pale green. The soln. contains some thiosulphate. R. E. Stevens represented the action of **sodium hydroxide** by the equation:  $8\text{FeS}_2 + 30\text{NaOH} = 4\text{Fe}_2\text{O}_3 + 14\text{Na}_2\text{S} + \text{Na}_2\text{S}_2\text{O}_3 + 15\text{H}_2\text{O}$ . In opening up pyrites for analysis, besides aqua regia or nitric acid, with or without bromine, H. C. Moore, K. List, and S. W. Parr recommend fusion with **sodium dioxide**; A. H. Low, treatment with a mixture of potassium hydrosulphate, tartaric acid, and sulphuric acid; O. Binder, fusion with a mixture of sodium carbonate and potassium nitrate; and W. C. Ebaugh and C. B. Sprague, fusion with a mixture of sodium carbonate and zinc oxide. According to G. Tammann and G. Bätz, the break in the heating curve of pyrites at  $684^{\circ}$  does not occur if calcium oxide be present; the liberated sulphur combines with the lime to form calcium sulphate and sulphide. A mixture of pyrites and lime is only slightly reduced when heated with wood charcoal. By the interaction of lime and pyrites a difficultly-reducible calcium iron oxysulphide is formed, and only a small quantity of ferrous oxide. P. Berthier found that when pyrites is heated with **lead oxide**, the mixture fuses and gives off sulphur dioxide; it requires 50 parts of lead oxide to 1 part of pyrites to expel all the sulphur. When 6 parts of lead oxide are used, two layers are produced—a lower layer of lead sulphide, and an upper layer of a mixture of lead and ferrous sulphides and oxides. F. Martin and O. Fuchs represented the reaction with **ferric oxide** by the equation:  $2\text{Fe}_2\text{O}_3 + 7\text{FeS}_2 = 11\text{FeS} + 3\text{SO}_2$ .

C. Doelter observed that with a 10 per cent. soln. of **sodium carbonate**, 7.08 per cent. dissolved from pyrite and 4.17 per cent. from marcasite; and H. N. Stokes found that if pyrite or marcasite be heated in a sealed tube with **sodium hydrocarbonate** at  $185^{\circ}$ , alkali sulphide and thiosulphate, and ferric oxide are formed. The reaction is in part reversible. If other carbonates of the heavy metals be present, the yield of thiosulphate is increased. The reaction of pyrite or marcasite with **copper carbonate** in the presence of alkali carbonate or hydrocarbonate, in a sealed tube at  $160^{\circ}$  to  $180^{\circ}$  for 14 hrs., is symbolized:  $2\text{FeS}_2 + 6\text{CuCO}_3 + 2\text{KHCO}_3 = 3\text{Cu}_2\text{S} + \text{Fe}_2\text{O}_3 + \text{K}_2\text{SO}_4 + 8\text{CO}_2 + \text{H}_2\text{O}$ . A similar result was obtained with **silver**



**carbonate.** J. W. Evans found that with water containing **calcium carbonate** in soln., pyrite and marcasite furnish hydrated ferric oxide. H. N. Stokes observed that with **zinc carbonate**,  $8\text{FeS}_2 + 14\text{ZnCO}_3 + 2\text{KHCO}_3 = 14\text{ZnS} + 4\text{Fe}_2\text{O}_3 + \text{K}_2\text{S}_2\text{O}_3 + 16\text{CO}_2 + \text{H}_2\text{O}$ , and with **lead carbonate**, the reaction was symbolized:  $8\text{FeS}_2 + 14\text{PbCO}_3 + \text{Na}_2\text{CO}_3 = 14\text{PbS} + 4\text{Fe}_2\text{O}_3 + \text{Na}_2\text{S}_2\text{O}_3 + 15\text{CO}_2$ . Since pyrite and marcasite produce ferric oxide when treated with zinc carbonate in alkaline soln., in the absence of oxygen, he assumed that the molecule is ferric sulphide in combination with sulphur  $\text{Fe}_2\text{S}_3(\text{S})$ . The sulphur reacts:  $4\text{S} + 3\text{Na}_2\text{CO}_3 = 2\text{Na}_2\text{S} + \text{Na}_2\text{S}_2\text{O}_3 + 3\text{CO}_2$ ; and  $\text{S} + \text{Na}_2\text{S} = \text{Na}_2\text{S}_2$ ; while the ferric sulphide reacts:  $\text{Fe}_2\text{S}_3 + 3\text{Na}_2\text{CO}_3 \rightleftharpoons \text{Fe}_2\text{O}_3 + 3\text{Na}_2\text{S} + 3\text{CO}_2$ . If the sulphide in soln. is removed by precipitation, as is the case when the reaction occurs in the presence of heavy metal carbonates, the reaction may proceed to an end. This shows how, in nature, pyrite may pass into hæmatite without oxidation.

J. Krutwig found that when pyrites mixed with **sodium chloride** is heated in a current of air, sodium sulphate, ferric chloride and oxide, and chlorine are evolved; if steam be present, hydrogen chloride and not chlorine is given off. A. P. Brown observed that at ordinary temp., cold or boiling, a 10 per cent. soln. of **copper sulphate** has very little action on pyrite or marcasite, but if the mixtures be heated in sealed tubes for 6 hrs. at  $200^\circ$ , all the iron of marcasite passes into soln. as ferrous sulphate, while with pyrite the product contains 2 mols of ferric sulphate for 1 mol of ferrous sulphate. He concluded therefore that the iron of marcasite is wholly in the ferrous condition,  $\text{Fe}''\text{S}_2$ , whilst that of pyrite is four-fifths ferric, and one-fifth ferrous,  $\text{Fe}''\text{S}_2(\text{Fe}'''\text{S}_2)_4$ . H. N. Stokes, however, found that at  $200^\circ$ , the soln. of copper sulphate decomposes marcasite more rapidly than pyrite; ferrous and ferric salts are formed in both cases, the former being found wholly in soln., the latter in the precipitate; there is no marked difference in the relative amounts of ferrous and ferric salts in either case; and the precipitate also contains cuprous sulphide and oxide, and possibly copper as well. The formation of a ferric salt is to be ascribed to the action of ferrous salt on the cupric salt, whilst some oxidation of sulphur to sulphuric acid occurs; and any ferric salt which is not precipitated will be reduced by the sulphides. The relative proportions of ferrous and ferric salts depend on the establishment of an equilibrium between the soln. and the products of the decomposition of the pyrite or marcasite, and not on any fundamental chemical difference in the two minerals. In the reaction with a neutral soln. of copper sulphate and marcasite or pyrite, at  $100^\circ$  to  $200^\circ$ , the sulphur is not completely oxidized since cupric and cuprous sulphides are formed:  $5\text{FeS}_2 + 14\text{CuSO}_4 + 12\text{H}_2\text{O} = 7\text{Cu}_2\text{S} + 5\text{FeSO}_4 + 12\text{H}_2\text{SO}_4$  in which 30 per cent. of the sulphur is oxidized; and  $4\text{FeS}_2 + 7\text{CuSO}_4 + 4\text{H}_2\text{O} = 7\text{CuS} + 4\text{FeSO}_4 + 4\text{H}_2\text{SO}_4$  in which 12.5 per cent. of the sulphur is oxidized. The reaction is more complex than this because of the interaction of the sulphides with the sulphate soln. E. G. Zies and co-workers found that when pyrite is heated in a sealed tube with a soln. of copper sulphate, covellite and chalcocite are formed. In the presence of quartz, 99.3 per cent. of the copper is converted to cuprous sulphide. The reaction was also studied by A. P. Brown, E. C. Sullivan, F. F. Grout, and G. S. Nishihara. When pyrite is similarly treated with a neutral soln. of **cupric chloride**, H. N. Stokes observed that the mineral is completely converted into ferrous salt and sulphuric acid with a corresponding reduction of the copper from the cupric to the cuprous state in accord with the equation:  $\text{FeS}_2 + 14\text{CuCl}_2 + 8\text{H}_2\text{O} = 14\text{CuCl} + \text{FeCl}_2 + 2\text{H}_2\text{SO}_4 + 12\text{HCl}$ . A. P. Brown observed that **silver nitrate** readily decomposes pyrite and marcasite forming ferrous and ferric salts; but the results with **silver sulphate** were indefinite. S. A. Kamenezky studied the action of silver nitrate. According to K. Kinoshita, when marcasite is boiled in a 3 per cent. silver nitrate solution, its surface tarnishes to tobacco-brown, then red, and finally blue, while pyrite becomes only slightly brownish. In the reaction, ferrous sulphate, sulphuric acid, and basic ferric sulphate are formed, but in different proportions for the two minerals. J. Lemberg found

that at 70° a sulphuric acid soln. of silver sulphate colours pyrite and marcasite reddish with a violet tinge, and in the cold some silver is formed. A. P. Brown said that a soln. of **gold chloride** is readily decomposed by marcasite and pyrite forming ferrous and ferric salts. According to W. Skey, marcasite and pyrite in soln. of silver or gold salts, at ordinary temp., are slowly covered with a film of silver or gold. Marcasite acts more rapidly than pyrite. These reactions were also examined by M. Leo, F. Zambonini, C. Palmer and E. S. Bastin, and S. Meunier. According to F. Martin and O. Fuchs, when pyrite mixed with **calcium sulphate** is heated to 700°, half the sulphur is evolved as sulphur dioxide, and a part is given off as sulphur. W. O. Hickok observed no reaction with a soln. of **stannous chloride**. According to H. N. Stokes, when marcasite or pyrite is heated with a soln. of **lead chloride**, in a sealed tube filled with carbon monoxide, for 12 hrs. at 180°, galena and lead sulphide are formed:  $4\text{FeS}_2 + 7\text{PbCl}_2 + 4\text{H}_2\text{O} = 7\text{PbS} + 4\text{FeCl}_2 + \text{H}_2\text{SO}_4 + 6\text{HCl}$ .

A. P. Brown studied the action of an aq. soln. of **potassium permanganate** on pyrite and marcasite, and found that the relative proportions of sulphur oxidized by 0.01*N*-KMnO<sub>4</sub>, and by 1, 3, and 5 per cent. soln. at different temp., were as follow:

Time (hrs.)	0.01 <i>N</i> -KMnO <sub>4</sub>		1 per cent. KMnO <sub>4</sub>		3 per cent. KMnO <sub>4</sub>		5 per cent. KMnO <sub>4</sub>	
	1	5	1	5	1	5	1	5
20° { Pyrite	0.78	1.72	1.72	1.80	1.65	2.81	2.39	2.79
{ Marcasite	1.07	2.38	1.22	2.23	2.72	2.83	2.10	3.39
100° { Pyrite	4.05	5.64	6.03	6.88	5.52	11.08	7.95	14.98
{ Marcasite	3.17	5.61	6.43	9.10	5.25	7.55	8.38	16.36

Whilst the total sulphur oxidized by the action of an excess of permanganate in a given time is greater in the case of marcasite than of pyrite, no relation was observed between the amount of sulphur oxidized and the quantity of mineral decomposed. H. N. Stokes found that an acidic soln. of potassium permanganate attacks marcasite more quickly than pyrite, but the difference is not great enough to be used as a means of measuring the relative proportions of the two minerals in a mixture.

L. L. de Koninck observed that **ferric salts**—ferric chloride or ammonium iron-alum—attack pyrite at 170° to 200°, forming a ferrous salt and sulphuric acid; whilst J. H. L. Vogt found that pyrite is slowly attacked by a 30 per cent. soln. of ferric chloride in the cold, forming a trace of sulphuric acid; and A. A. Julien observed that a soln. of ferric chloride is reduced by marcasite. F. A. Eustis said that with pyrite, the reaction:  $2\text{FeCl}_3 + \text{FeS}_2 = 3\text{FeCl}_2 + 2\text{S}$  is 40 per cent. off completion. According to R. J. Traill and W. R. McClelland, a soln. of ferric chloride attacks pyrrhotite but not pyrite. The reaction was studied by E. Kopp, W. F. Hillebrand and H. N. Stokes, G. S. Nishihara, and F. F. Grout. H. N. Stokes found that boiling dil. soln. of ferric salts attack pyrite rapidly, the action is slow, but appreciable, with cold soln., and the difference in the effects with pyrite and marcasite are so marked that the reaction can be utilized quantitatively for determining the proportions of the two minerals in a mixture. The method was also examined, and employed by E. T. Allen and co-workers—*vide supra*. The reaction may be regarded as taking place in two stages:  $\text{FeS}_2 + \text{Fe}_2(\text{SO}_4)_3 = 3\text{FeSO}_4 + 2\text{S}$ ; and  $2\text{S} + 6\text{Fe}_2(\text{SO}_4)_3 + 8\text{H}_2\text{O} = 12\text{FeSO}_4 + 8\text{H}_2\text{SO}_4$ . A soln. containing a gram of ferric iron per litre in the form of ammonium ferric alum is a convenient strength to employ. The percentage of sulphur oxidized varies with the concentration of the ferric salt, so that the percentage decreases as the reduction proceeds. Thus:

Pyrite	{ Fe reduced	.	.	67.8	88.7	95.2	100
	{ S oxidized	.	.	71.4	65.2	63.2	60.4
Marcasite	{ Fe reduced	.	.	69.2	78.5	100.0	
	{ S oxidized	.	.	23.2	22.5	16.2	

and at 20° and 100° the percentages of sulphur oxidized when the reduction was

completed were respectively 80.8 and 60.4 with pyrite, and 30.6 and 17.4 with marcasite. The general results show that when pyrite or marcasite is boiled with an excess of a soln. of ferric salt until the reaction is complete, the ratio of sulphur oxidized to mineral decomposed is definite and characteristic of each mineral when standard conditions are employed. The amount of sulphur oxidized in pyrite is about 60.4 per cent. and in marcasite about 18.0 per cent. of the total sulphur. These figures are called the *characteristic oxidation coefficients*.

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### § 43. Ferrous Sulphate

In the first century of our era, Dioscorides, in his *Περὶ ὕλης ἰατρικῆς*, used the term *χαλκανθον*, *chalcanthon*,—from *χαλκός*, copper; *ἄνθος*, flower—which is what was later called **vitriol**. He said (5. 74) :

Chalcanthum is a solidified liquid which appears in three forms. One kind is produced from the liquidus which trickle down drop by drop, and congeal in certain mines, and hence the Cyprian miners call it *stalactis*, and Petesius called it *pinarion*. A second kind collects in certain caverns, and is afterwards poured into trenches, where it congeals, whence it derives its name *pectos*. The third kind is called *hepenthon*, and it is made mostly in Spain. It has a beautiful colour, but is weak. It is prepared by digesting it with water, boiling the liquid, and then transferring it to tanks to settle. After some days, it congeals and separates into many small pieces, having the form of dice, which stick together like grapes. The most valuable kind is blue, heavy, dense, and translucent.

Contemporaneously with Dioscorides, Pliny, in his *Historia naturalis* (36. 32), designated the same substance *atramentum sutorium*. The literal meaning of the term is "shoemaker's blacking," and these words were used because the substance was employed for blackening leather. Pliny said :

The name *chalcanthum* given by the Greeks to *atramentum sutorium* shows that they recognized its relationship to copper. There is no substance of an equally miraculous nature. It is made in Spain from wells of this kind of water. This water is boiled with an equal quantity of pure water, and then poured into wooden tanks (fish-ponds). Across these tanks are fixed beams, to which hang cords stretched by little stones. Upon these cords adheres the *limus* in drops of a vitreous appearance, somewhat resembling a bunch of grapes. After removal, it is dried for about thirty days. It is of a blue colour, and of a brilliant lustre. It is very like glass. Its solution is the blacking used for colouring leather. Chalcanthum is made in many other ways. Its kind of earth is sometimes dug from ditches, from the sides of which exude drops, which solidify by the winter frosts into icicles, called *stalagmia*, and there is none more pure. When its colour is nearly white, with a slight tinge of violet, it is called *leukvion*. It is also made in rock basins, the rain-water collecting the *limus* into them, where it becomes hardened. It is also made, in the same way as salt, by the intense heat of the sun. Hence it is that some distinguish two kinds, the mineral, and artificial. The latter is paler than the former, and is as much inferior to it in quality as it is in colour.

According to K. B. Hofmann,<sup>1</sup> the *chalkanthon* or *chalkanthos* of the ancients was iron-vitriol contaminated with copper sulphate, and J. Berendes said that probably the same substance was called *chalcites*; whilst the fourth-century writer Marcellus Burdigallensis applied the term *chalcanthum viride cyprium* to *atramentum sutorium*. This compound was also described in the second century by C. Galen, in his *De compositione medicamentorum*; and, according to E. Darmstädter, it is alluded to in Geber's *De investigatione perfectionis*.

The term *vitriol* is mentioned in a work on chemical technology—*Compositiones ad tingenda*—dating, probably, from the beginning of the eighth century; and the term is used for an impure ferrous sulphate. The word was employed by Albertus Magnus, who, early in the thirteenth century, in the fifth book of his *De rebus metallicis et mineralibus*, said that *atramentum viride a quibusdam vitreolum vocatur*—"the term *vitriol* is applied to green atrament" (ferrous sulphate)—so that G. Agricola could say, in his *De natura fossilium* (Basileæ, 213, 1546), that in recent years the name *vitriolum* has been applied to this substance. The term *vitriol* comes from the Latin *vitrium*, glass, in allusion to the glassy appearance of the crystals of the vitriols. Although Pliny emphasizes the blue colour of vitriol (copper sulphate), his solution for colouring leather was almost certain to have been ferrous sulphate. Both iron and copper sulphates were thus known to the Romans, but the two substances were not clearly distinguished the one from the other. G. Agricola said that there are three varieties of *atramentum sutorium*—*viride* (green), *cæruleum* (blue), and *candidum* (white). These no doubt respectively indicate ferrous, copper, and zinc sulphates. The pseudonymous Basil Valentine, in the sixteenth or seventeenth century, in his *Von den natürlichen und ubernatürlichen Dingen* (Leipzig, 1624), said that when mars (iron) is dissolved in oil of vitriol *vitriol of Mars* is formed; and in his *Letztes Testament* (Strassburg, 1651), as well as his *Haliographia* (Bononiæ, 1644), he said:

Calcine a mixture of equal parts of the filings of Mars and sulphur in a brick kiln until the colour is purple, then pour on it distilled water or vinegar which extracts a green colour. Abstract two parts of that water, and let it shoot (crystallize). Thus you have noble vitriol. . . . Return thanks to God, the creator of minerals, metals, and all other things.

G. Agricola, in his *De re metallica* (Basileæ, 1556), said that vitriol can be made by four different processes. In two of these methods mine-water containing vitriol is collected either by means of buckets or by pumping and evaporating in pits as described by Dioscorides, and Pliny. In a third method, *melanteria*, *sory*, *chalcitis*, or *misy*—preferably the two former—was weathered, the soluble matters extracted with water, and the solution evaporated for crystallization. According to H. C. and L. H. Hoover, the term *misy* referred to a yellow, ochreous material, and *sory*, a blackish stone, both impregnated with vitriol; *chalcitis* referred to partially decomposed pyrites, and *melanteria*—from μέλαν, ink—to a native vitriol—the modern melanerite, hydrated ferrous sulphate. J. D. Dana suggested that *misy*

was in part copiapite, a basic ferric sulphate. G. Agricola's objections to misy and chalcite may have been due to their copper contents. The fourth method, from vitriolic earth or stones, is thus described :

The ore is at first carried and heaped up, and is then left for five or six months exposed to the rain of spring and autumn, to the heat of summer, and to the rime and frost of winter. It must be turned over several times with shovels, so that the part at the bottom may be brought to the top, and it is thus ventilated and cooled ; by this means the earth crumbles up and loosens, and the stone changes from hard to soft. Then the ore is covered with a roof, or else it is taken away and placed under a roof, and remains in that place six, seven, or eight months. Afterwards as large a portion as is required is thrown into a vat, which is half-filled with water ; this vat is one hundred feet long, twenty-four feet wide, eight feet deep. It has an opening at the bottom, so that when it is opened the dregs of the ore from which the vitriol comes may be drawn off, and it has, at the height of one foot from the bottom, three or four little holes, so that, when closed, the water may be retained, and when opened the solution flows out. Thus the ore is mixed with water, stirred with poles and left in the tank until the earthy portions sink to the bottom and the water absorbs the juices. Then the little holes are opened, the solution flows out of the vat, and is caught in a vat below it ; this vat is of the same length as the other, but twelve feet wide and four feet deep. If the solution is not sufficiently vitriolous it is mixed with fresh ore ; but if it contains enough vitriol, and yet has not exhausted all of the ore rich in vitriol, it is well to dissolve the ore again with fresh water. As soon as the solution becomes clear, it is poured into the rectangular leaden caldron through launders, and is boiled until the water is evaporated. Afterwards as many thin strips of iron as the nature of the solution requires, are thrown in, and then it is boiled again until it is thick enough, when cold, to congeal into vitriol. Then it is poured into tanks or vats, or any other receptacle, in which all of it, apt to congeal, does so within two or three days. The solution which does not congeal is either poured back into the caldron to be boiled again, or it is put aside for dissolving the new ore, for it is far preferable to fresh water. The solidified vitriol is hewn out, and having once more been thrown into the caldron, is re-heated until it liquefies ; when liquid, it is poured into moulds that it may be made into cakes. If the solution first poured out is not satisfactorily thickened, it is condensed two or three times, and each time liquefied in the caldron and re-poured into the moulds, in which manner pure cakes, beautiful to look at, are made from it.

The oxidation of pyrites has been previously described. N. Lemery discussed the contamination of iron-vitriol with copper-vitriol, and J. F. Vignani obtained green iron-vitriol by the action of iron on blue copper-vitriol until all the copper is precipitated from the soln. by the metallic iron. N. Lemery showed that a mixture of sulphur and iron-filings in contact with water becomes heated—*vide supra*, chemical properties of iron—and N. Lefèvre observed that when a mixture of iron-filings and sulphur is weathered, iron-vitriol is formed. Crystals of *vitriolum martis* were prepared by J. R. Glauber, and G. E. Stahl, in the seventeenth and eighteenth centuries, by evaporating a soln. of iron in sulphuric acid.

The transformation of iron pyrites into iron-vitriol by weathering was a puzzle to the early chemists, and the history was discussed by H. Kopp, and E. O. von Lippmann. In 1669, J. Mayow had the right explanation, for he said that the acid spirit of which vitriols are composed seems to be produced by the action of the nitro-aerial spirit on the sulphur of pyrites, the acid spirit then unites with the iron to form vitriol. He added :

Vitriols are produced from the stone or rather the saline-sulphureous earth usually called marchasite (pyrites), and from it on the application of fire the flowers of common sulphur are elicited in considerable abundance. But after this earth has been exposed for some time to the air and wet weather and then (as its nature is) has fermented spontaneously, it will be found to be richly impregnated with vitriol. No doubt the nitro-aerial spirit, effervescing with the metallic sulphur of these marchasites, converts their more fixed part into an acid liquid, which, directly it is produced, attacks the metallic particles of the said stone and draws them out and at last coalesces with them to form vitriol.

J. F. Henckel supposed that the pyrites abstracts salty or acidic particles from the air, and is thus converted into vitriol ; and G. Brandt, that the pyrites, by taking up moisture from the air, passes into vitriol. The advocates of the phlogiston theory—*e.g.*, G. A. Scopoli—believed that the conversion of pyrites to vitriol was a process involving the removal of phlogiston, but A. L. Lavoisier proved that oxygen

is absorbed by the pyrites whereby it is converted into vitriol. In other words, *the oxidation of the sulphide—pyrites—transforms it into a sulphate—vitriol*. This interpretation of the phenomenon of the weathering of pyrites was generally accepted as the antiphlogiston doctrine and became the dominant theory in chemistry.

It was observed that an aq. soln. of vitriol becomes turbid when it is exposed to the air. T. Bergman showed that this is due to the absorption of oxygen from the atmosphere so that the iron in the soln. becomes a stronger calx. In this state, it requires more acid to maintain it in soln. This, by the antiphlogiston theory, means that the ferrous sulphate in soln. is oxidized by exposure to air forming ferric sulphate. J. L. Proust, however, established the existence of two iron sulphates as chemical individuals. He showed that the green sulphate contains 27 per cent. of oxygen, whilst the red variety contains 48 per cent. The green, lower sulphate came to be called **ferrous sulphate**,  $\text{FeSO}_4 \cdot n\text{H}_2\text{O}$ , and the red, higher sulphate, **ferric sulphate**,  $\text{Fe}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$ . J. L. Proust showed that the chemical properties of the two sulphates are quite different, and that oxidizing agents—*e.g.*, nitric acid—convert ferrous into ferric sulphate, whilst reducing agents—like hydrogen sulphide—convert ferric into ferrous sulphate.

Two hydrated ferrous sulphates occur in nature—the monohydrate, and the heptahydrate. The heptahydrate occurs in two crystalline forms. Analyses of natural waters carrying ferrous sulphate in solution were reported by T. Pusch,<sup>2</sup> H. Bley, L. von Barth and R. Wegscheider, J. C. Essener, G. C. Wittstein, and N. O. Hamberg. Ferrous sulphate often accompanies pyrite as an efflorescence—*e.g.*, at Copperas Mountain, Ohio, where it is associated with alum and pyrite. It also occurs in solution in many mine-waters where it has been formed by the oxidation of pyrite or marcasite. When the water has had the opportunity of concentrating, monoclinic crystals of heptahydrated ferrous sulphate are formed. This has taken place in the mine at Goslar, Harz; at Bodenmais, Bavaria; Falun, Sweden; Hurlet, Scotland; and many other places. The mineral so formed was called *atramentum viride* by C. Gesner; *vitriolum viride*, or *vitriolum ferri*, or *vitriolum martis*, by J. G. Wallerius; *mélantérie*, by F. S. Beudant, and this was altered to **melanterite**, its present name; *luckite*, by A. Carnot; and *alcaparroza verde*, by A. Raimondi. This is probably the salt described by the ancient writers indicated above, and it is and has been also called *copperas*, and *green vitriol*. A rare rhombic form of the heptahydrate was reported by G. H. O. Volger to occur at Windgälle in the Swiss Canton Uri—*i.e.* the *Pagus tauriscorum* of the Romans; and the mineral was accordingly called **tauriscite**. It was also observed by J. A. Krenner to occur at Schmöllnitz, Slovakia. J. B. Macintosh described an impure monohydrate from Chile, and R. Scharizer applied the term **ferropallidite**, to a sample from Alcapa Rossa, Calama, Chile; and J. A. Krenner called a sample from Schmöllnitz, Slovakia, *schomolnokite*.

Analyses of melanterite were reported by W. T. Schaller,<sup>3</sup> G. Vavrinecz, J. Janowsky, J. Thiel, J. E. Edgren, E. Manasse, A. Frenzel, V. Zsivny, A. Carnot, and L. Michel, and the results correspond with monoclinic, heptahydrated ferrous sulphate,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ . The analysis of tauriscite reported by G. H. Volger, and J. A. Krenner, agree with the assumption that the rhombic crystals are also heptahydrated ferrous sulphate. The analysis of ferropallidite or schomolnokite, reported by R. Scharizer, and J. Donau, agree that the mineral is monohydrated ferrous sulphate,  $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ . Analyses of ferrous sulphate were made by T. Thomson.

**The preparation of ferrous sulphate.**—G. Tammann<sup>4</sup> noted that anhydrous ferrous sulphate is formed when a mixture of lead sulphate and iron is heated to about  $540^\circ$ ; the reaction is turbulent, and is symbolized:  $\text{PbSO}_4 + \text{Fe} = \text{Pb} + \text{FeSO}_4 + <11 \text{ Cals.}$  L. Hackspill and co-workers noted that it is formed in a similar way by heating iron with an excess of alkali sulphate. B. Neumann observed that ferrous sulphate is formed when a mixture of sulphur dioxide and oxygen acts on ferrous oxide:  $\text{Fe}_3\text{O}_4 + 2\text{SO}_2 + \text{O}_2 \rightleftharpoons \text{FeSO}_4 + \text{Fe}_2\text{O}_3 + \text{SO}_3$ ; and ferrous sulphate



may be regarded as an intermediate stage in the catalytic action of iron oxide in the oxidation of sulphur dioxide to the trioxide. According to G. Keppeler, some ferric oxide is formed. The Farbwerke vorm. Meister Lucius und Brüning, and J. d'Ans suggested that ferrous sulphite is formed as a transient intermediate product, and that this is oxidized to the sulphate. G. Keppeler and J. d'Ans noted that ferrous sulphate is formed when sulphur dioxide acts on ferric sulphate:  $\text{Fe}_2(\text{SO}_4)_3 + \text{SO}_2 \rightleftharpoons 2\text{FeSO}_4 + 2\text{SO}_3$ . R. Cox discussed the formation of ferrous sulphate when hydrogen sulphide acts on ferric oxide or hydroxide in the purification of coal-gas. E. T. Allen and co-workers noticed that ferrous sulphate is formed when pyrrhotite, marcasite, or pyrite is triturated in a mortar, or heated in air to  $100^\circ$ ; E. Kothny, when pyrite is heated in air to  $250^\circ$  to  $290^\circ$ ; and H. Saito, P. Truchot, and A. W. Warwick also noted that ferrous sulphate is formed as an intermediate or by-product in the oxidation of pyrites—F. Warlimont observed that with pyrrhotite, the formation of ferrous sulphate begins about  $400^\circ$ , and at  $420^\circ$ , to  $430^\circ$ , 11.0, 15.6, and 20.2 per cent. were formed respectively in 3, 4, and 5 hrs. J. Kolb noted the formation of ferrous sulphate when pyrite is heated with copper oxide in air; and V. Tafel and E. Greulich, when chalcopyrite is heated above  $300^\circ$ .

R. Brandes, and F. Stolba showed that hydrated ferrous sulphate can be dehydrated at a suitable temp. A. Adolphs, and F. Krafft found that the salt is dehydrated in the high vacuum of the cathode light at  $280^\circ$ ; H. Saito, K. Friedrich, and K. Friedrich and A. Blicke observed a break in the time-temp. curve when hydrated ferrous sulphate is heated in air, and this corresponds with the passage of the monohydrate to the anhydrous salt. T. E. Thorpe and J. I. Watts heated the hydrate in hydrogen to prevent oxidation—H. Precht and K. Kraut recommended  $100^\circ$ ; E. Kothny,  $250^\circ$ ; J. Kendall and A. W. Davidson,  $270^\circ$ ; J. Kendall and A. W. Davidson, and F. Warlimont,  $290^\circ$ ; J. d'Ans, and G. Keppeler and J. d'Ans,  $300^\circ$  to  $320^\circ$ ; and J. A. Hedvall and J. Heuberger,  $300^\circ$  in carbon dioxide. R. de Forcrand observed that in hydrogen, the last mol. of water is slowly expelled at  $180^\circ$ , but recommended  $250^\circ$  for the completion of the action; he added that about 1.5 per cent. of a basic sulphate is unavoidably formed at the same time. E. Greulich said that all the water is not expelled from ferrous sulphate in hydrogen even at  $200^\circ$ , and that 1.9 per cent. of ferric sulphate is formed; he recommended treating ferrous chloride with 100 per cent. sulphuric acid in an atm. of hydrogen, and driving off the excess of sulphuric acid at  $230^\circ$  in an atm. of hydrogen. T. Bolas, and A. Bussy and L. R. Lecanu obtained what they regarded as the anhydrous salt by treating the hydrated salt at ordinary temp. with sulphuric acid of sp. gr. 1.843. E. Howl and F. Perry also recovered the salt in the anhydrous form from acidic liquors by evaporating the lye to a concentration of 75 per cent. free sulphuric acid. A. C. Knowles evaporated the soln. of ferrous sulphate by spraying it in hot air or hot gas.

**The hydrated forms of ferrous sulphate.**—J. R. Glauber, and G. E. Stahl prepared a soln. of ferrous sulphate by dissolving iron in sulphuric acid until the acid is saturated, and evaporating the filtered soln. for crystallization. Ferrous sulphate absorbs oxygen from the air so readily that the crystals obtained by evaporating the aq. soln. are liable to be contaminated with ferric sulphate. P. A. von Bonsdorff recommended saturating dil. sulphuric acid (1:4 or 1:5) with iron by boiling the mixture in a narrow-necked flask until it is near the point of crystallization. The liquid is then strained through a filter, moistened with water, into a vessel rinsed out with dil. sulphuric acid. The acid prevents the liquid from hydrolysis, and the funnel should have a long neck reaching to the bottom of the vessel. The crystals are allowed to drain, and dried by pressure between bibulous paper at  $30^\circ$ . P. Geiseler, and A. Piccini and F. M. Zuco employed a similar process. E. Cohen and A. W. Visser tried to prevent the oxidation of the soln. by using an atm. free from air in a Soxhlet's apparatus and air-free water. C. L. Mayer electrolyzed soln. of alkali sulphate or hydrosulphate with electrodes

of iron, or of oxide or carbonate minerals, and obtained soln. from which hydrated ferrous sulphate could be obtained by crystallization.

W. Kistiakowsky noticed that when a strip of iron is dipped in a 2 per cent. soln. of sodium sulphate and exposed to air containing carbon dioxide, the iron is eroded near the interface of air and soln. to form sodium carbonate and ferrous sulphate. A soln. of ferrous sulphate is formed when ferrous oxide or hydroxide is dissolved in sulphuric acid. J. Behrens observed that a slurry of gypsum and freshly-precipitated ferrous hydroxide reacts in an atm. of carbon dioxide to form ferrous sulphate:  $\text{FeO} + \text{CO}_2 + \text{CaSO}_4 = \text{CaCO}_3 + \text{FeSO}_4$ . I. Sorganuma noticed that the sulphurous gases from mineral springs act on ferruginous rocks and clays producing melanterite. G. C. Westby, and D. Peniakoff described processes for using sulphurous, waste gases from the industries for making ferrous sulphate soln. C. Winkler, and G. Agde also utilized waste acid, or acid from the lead chambers for preparing ferrous sulphate from iron; and instead of using iron, A. Buisine used incompletely roasted pyrites; the waste oxide from aniline works; A. Pezzolato, pyrite reduced by preheating with carbon; G. Meunier, artificial ferrous sulphide; G. Kogan, and C. Mène, blast-furnace slags; and T. Ritterhaus, spathic iron ore.

J. J. Berzelius obtained a soln. free from ferric salt by dissolving ferrous sulphide in sulphuric acid. A. L. Day obtained mixed copper and ferrous sulphates by the action of dil. sulphuric acid on bornite, or on mixtures of pyrrhotite and chalcocite or covellite. The formation of ferrous sulphate as a stage in the weathering of iron pyrites is a very old process—*vide supra*. It was discussed by A. P. Brown, E. Dittler, T. J. Drakeley, S. H. Emmens, W. Haidinger, A. Lacroix, J. Lefort, W. Thörner, and A. Wurm. E. T. Allen and co-workers obtained a soln. of ferrous sulphate by the action of marcasite or pyrite on a soln. of ferric sulphate; and A. Hutin represented the reaction:  $\text{Fe}_2(\text{SO}_4)_3 + \text{FeS}_2 + 2\text{O}_2 = 3\text{FeSO}_4 + 2\text{SO}_2$ ; and  $\text{Fe}_2(\text{SO}_4)_3 + \text{FeS}_2 + 4\text{H}_2\text{O} = 3\text{FeSO}_4 + 2\text{SO}_2 + 4\text{H}_2$ . A. and P. Buisine also reduced a soln. of ferric sulphate with iron:  $\text{Fe}_2(\text{SO}_4)_3 + \text{Fe} = 3\text{FeSO}_4$ . T. von Grotthus found that an alcoholic soln. of ferric sulphate is reduced to ferrous sulphate in a closed vessel by exposure to light; W. H. Ross obtained a similar result by exposing a soln. of sugar and ferric sulphate to ultra-violet light; and A. Kailan, by exposing the soln. to radium rays. W. Feld also discussed the formation of ferrous sulphate by heating soln. of the polythionic acids.

O. Mustad recommended preparing a soln. of ferrous sulphate by dissolving the hydrated salt in water acidified with sulphuric acid, and allowing the soln. to stand for some weeks in contact with iron so as to neutralize the acid, and keep the salt in the ferrous state. A. F. W. von Escher triturated the hydrated salt with reduced iron, dissolved it in water at 60° through which a current of hydrogen was passed, removed the free acid with baryta-water, and allowed the mixture to stand a few days. N. A. Tananaeff dissolved the hydrated salt in boiled water saturated with carbon dioxide, added hydrogenized palladium, and kept the soln. in an atm. of hydrogen; F. W. Horst treated the hot soln. with hydrogen sulphide gas, and then with carbon dioxide. G. Bailhache observed that the aq. soln. can be preserved for a long time in an atm. of carbon dioxide. F. W. Horst said that the soln. can be kept from oxidation, for a short time, by covering it with a layer of benzene.

The pickling of iron with acids, and in some wet processes of extracting products from ferruginous ores, furnishes as waste-products acidic liquors containing ferrous sulphate in soln., and from which the salt can be recovered. This subject was discussed by Bergbau Aktien Gesellschaft Friedrichsseen, S. E. Coburn, G. Agde, E. V. Chambers and co-workers, C. A. Hall, L. Hirt, A. C. Knowles, L. Kugel, L. Simmonds, H. Stähler, H. C. Stewart, L. Thorel, and G. Weintraub.

According to P. A. von Bonsdorff, commercial ferrous sulphate, or green vitriol, or copperas may be contaminated with ferric, cupric, zinc, manganese, tin,

aluminium, magnesium and calcium sulphates, and arsenious acid. The copper and ferric salts can be removed by digesting a soln. of the salt in sulphuric acid with metallic iron, or ferrous sulphide, out of contact with air; the arsenic, copper, and tin can be removed by allowing the soln. saturated with hydrogen sulphide to stand for some days before filtering. H. Wurtz recommended removing copper and ferric salts by digesting the soln. with barium carbonate; and L. Thorel removed zinc and manganese by boiling the soln. with potassium hydrotartrate. The subject was also discussed by C. H. Butcher, E. Merck, and F. Mach and P. Lederle.

The crystals which separate from the aq. soln. at ordinary temp. are the **heptahydrate**,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , and, according to F. Fränckel, the same salt separates from

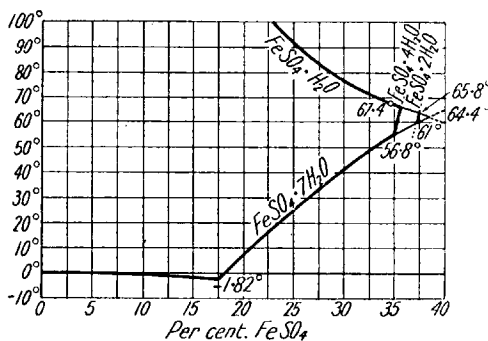


FIG. 640.—Percentage Solubility of Ferrous Sulphate in Water.

an aq. soln. between  $-1.821^\circ$  and  $56.7^\circ$  with soln. containing 14.91 to 35.06 per cent. of  $\text{FeSO}_4$ —*vide infra*, Fig. 640. This hydrate is also called *green vitriol*, *copperas*, and *vitriolum martis*. F. Wirth, and F. B. Kenrick studied the conditions under which the heptahydrate separates from soln. containing sulphuric acid—*vide infra*, Fig. 640. R. Brandes observed that the heptahydrate is formed when the crystals of one of the lower hydrates, or of the anhydrous salt are exposed to moist air. H. Seymour discussed the continuous crystallization of the salt in the course of its manufacture. The crystals of the heptahydrate were analyzed by J. J. Berzelius, T. Bergman, R. Kirwan, F. Thomas, E. Mitscherlich, and T. Graham; the analyses of melanterite have been previously indicated. J. B. Berthelot recommended purifying the crystals by allowing the salt to crystallize from water acidulated with sulphuric acid; then boiling 500 parts of the crystals with 550 parts of water, and 8 parts of iron turnings; filtering the boiling soln. into a mixture of 375 parts of alcohol of sp. gr. 0.84, and 8 parts of sulphuric acid with constant stirring; straining the cold liquid from the small crystals which form; draining the crystals on linen; and drying them between bibulous paper, constantly renewed. The alcohol retains in soln. any ferric salt which may be present, and the solubility of that salt is increased by the sulphuric acid. N. A. Tananaeff recommended washing out the alcohol by boiled water saturated with carbon dioxide. Processes were also described by F. Fränckel, E. Jordis and H. Vierling, L. Thorel, G. Ruspini, and H. Vierling.

A. F. de Fourcroy found that cold water dissolves nearly half its weight of the heptahydrate, and boiling water very nearly its own weight. Observations were also made by A. Ure, T. Bergman, E. Tobler, H. G. Greenish and F. A. U. Smith, and R. Brandes and E. Firnhaber. H. Schiff found that a soln. sat. at  $15^\circ$  contains 37.2 per cent. of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ; C. von Hauer, 17.02 per cent.  $\text{FeSO}_4$  at  $11^\circ$  to  $14^\circ$ ; W. Stortenbeker, 26.69 per cent.  $\text{FeSO}_4$  at  $25^\circ$ ; F. Wirth gave 22.84 per cent.  $\text{FeSO}_4$  at  $25^\circ$ ; G. Agde and H. Barkholt, 13.80 at  $1^\circ$ ; 17.10 at  $9.6^\circ$ ; 21.30 at  $21^\circ$ ; 22.98 at  $25^\circ$ ; 26.56 at  $34^\circ$ ; 30.04 at  $43^\circ$ ; 34.50 at  $54^\circ$ ; and 30.20 at  $80^\circ$ ; and V. J. Occleshaw, 22.98 at  $25^\circ$ . F. A. H. Schreinemakers found 24.9 per cent.  $\text{FeSO}_4$  at  $30^\circ$ . R. Brandes observed that the increase in the solubility of the salt with a rise of temp. continues up to  $87.5^\circ$ , and thereafter the solubility decreases with a rise of temp. He attributed this to hydrolysis whereby a white product is formed. A transition point at about  $63.5^\circ$  was observed by G. J. Mulder; at  $64^\circ$  by W. A. Tilden; and at  $65^\circ$  by A. Étard. I. Koppel thought there

was one at 40°. A. Étard gave for the percentage solubility,  $S$ , per cent.  $\text{FeSO}_4$ :

	-1°	24°	52°	60°	67°	94°	102°	112°	130°	152°
$S$	13.0	22.7	32.5	36.4	37.7	36.7	34.7	28.0	17.3	2.5

so that from -2° to 65°,  $S=13.5+0.3788\theta$ ; from 65° to 98°,  $S=37.5$ , i.e. a constant; from 98° to 156°,  $S=37.5-0.6685\theta$ ; and at 156°, the salt is practically insoluble. F. Fränckel obtained for the percentage solubility:

$S$	-0.685°	-1.824°	0°	20.10°	50.21°	56.7°	60.01°	64.00°	68.02°	90.13°
	5.1811	14.91	13.53	21.00	32.71	35.06	35.46	35.65	35.96	27.15

Solid phase      Ice                       $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$                        $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$                        $\text{FeSO}_4 \cdot \text{H}_2\text{O}$

There is a region of metastability for the tetrahydrate when at 65.00° and 70.04°, the respective values of  $S$  are 35.73 and 35.93 per cent.  $\text{FeSO}_4$ . F. K. Cameron considers that the solid phase above 67.4° is not, as indicated by F. Fränckel, the monohydrate, but rather the dihydrate. According to F. Fränckel, the **eutectic temperature**, at -1.824° and 14.91 per cent. of  $\text{FeSO}_4$ , was given by F. Guthrie at -2°, with 16.95 per cent. of  $\text{FeSO}_4$ . I. Koppel gave -2°; H. Gröber, -1.8°; and E. W. Washburn and E. R. Smith, -1.80°. According to F. Fränckel, the **transition temperature** for the hepta- and tetrahydrates:  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O} \rightleftharpoons \text{FeSO}_4 \cdot 4\text{H}_2\text{O} + 3\text{H}_2\text{O}$  occurs at about 56.7°; and for the tetra- and monohydrates:  $\text{FeSO}_4 \cdot 4\text{H}_2\text{O} \rightleftharpoons \text{FeSO}_4 \cdot \text{H}_2\text{O} + 3\text{H}_2\text{O}$ , at about 64°. There is here no evidence of the formation of the alleged hexa-, penta-, tri-, and dihydrates. In agreement with these observations by F. Fränckel, W. Müller-Erzbach found evidence of the mono-, tetra-, and heptahydrates on his vap. press. curves. This also agrees with observations on the system:  $\text{FeSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$  indicated below. On the other hand, F. K. Cameron observed as an average on a rising and falling temp., breaks corresponding with transitions at 56.8°, 61.0°, 64.4°, 65.8°, and 67.8°. These breaks, along with the solubility data of F. Fränckel, F. Wirth, A. Étard, F. A. H. Schreinemakers, and G. Agde and H. Barkholt, are interpreted by the solubility curve, Fig. 640. The hydrates were studied by E. N. Gapon.

L. de Boisbaudran reported the **hexahydrate**,  $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ , to be formed when a soln. of ferrous sulphate, slightly under-saturated with respect to the heptahydrate, is seeded with a crystal  $\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$  obtained from the aq. soln. at 50°. C. Hensgen obtained the hexahydrate by treating the heptahydrate with conc. hydrochloric acid; T. Bolas, by exposing the pyrosulphate to moist air; E. Wiedemann, by melting the heptahydrate at 65° and removing the molten portion; and F. Jeremin obtained colourless plates from a sulphuric acid soln. of ferrous sulphate. E. Cohen and A. W. Visser, L. Rolla, W. C. Schumb, and H. Schottky assumed that the hexahydrate has a real existence, but R. de Forcrand had doubts. In any case, the green, acicular crystals of the hexahydrate are metastable, and soon pass into the heptahydrate.

According to J. C. G. de Marignac, when a soln. of ferrous sulphate in sulphuric acid is evaporated in vacuo, the heptahydrate first separates, then the **pentahydrate**,  $\text{FeSO}_4 \cdot 5\text{H}_2\text{O}$ , and finally the tetrahydrate. F. K. Cameron doubted if this is an accurate description of the facts. L. de Boisbaudran found that when a soln. of ferrous sulphate is seeded with pentahydrated copper sulphate, pentahydrated ferrous sulphate separates as a metastable phase which is rapidly transformed into the heptahydrate; he added that the pentahydrate is difficult to prepare and it can be obtained only from soln. much supersaturated with respect to the heptahydrate. J. T. Conroy supposed this salt to be present in conc. sulphuric acid soln. of the heptahydrate; and T. Bolas, and J. B. Hannay considered it to be formed by the dehydrating action of sulphuric acid. A. Schrauf reported the pentahydrate to occur in nature in needle-like crystals along with melanterite, and he called the mineral **siderotile**. R. de Forcrand, F. K. Cameron, F. K. Cameron and H. D. Crockford, and G. Agde and H. Barkholt expressed doubts as to the existence of the pentahydrate.

As just indicated, J. C. G. de Marignac considered that when an acidic soln. of ferrous sulphate crystallizes in vacuo, the last crop of crystals is the **tetrahydrate**,  $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ . P. A. von Bonsdorff obtained the tetrahydrate in a similar manner; and H. V. Regnault, by evaporating a soln. of ferrous sulphate at  $80^\circ$ . F. Fränckel showed the conditions of stability of the tetrahydrate, Fig. 640, in aq. soln.; and F. B. Kenrick, the conditions of equilibrium in sulphuric acid soln.—*vide supra*, Fig. 640. F. Fränckel showed that in aq. soln., the salt is stable between  $56.7^\circ$  and  $64.0^\circ$ , and metastable between  $64.0^\circ$  and  $70.04^\circ$ . J. B. Hannay obtained the tetrahydrate by the progressive dehydration of the heptahydrate; and P. A. von Bonsdorff, E. Moles and M. Crespi, J. T. Conroy, W. Müller-Erbach, R. Scharizer, H. O. Hofman and W. Wanjukoff, C. Gaudefroy, R. de Forcrand, and T. E. Thorpe and J. I. Watts obtained this hydrate in a somewhat similar manner.

According to O. B. Kühn, the **trihydrate**,  $\text{FeSO}_4 \cdot 3\text{H}_2\text{O}$ , is formed as a white crust when a soln. of ferrous sulphate is mixed with a large excess of sulphuric acid; and, according to R. J. Kane, when a soln. of ferrous sulphate, saturated with hydrogen chloride, is allowed to cool. The green crystals of the heptahydrate are mixed with the pale green crystals of the trihydrate. T. Bolas reported the same hydrate to be formed by the action of sulphuric acid on the heptahydrate; and J. B. Hannay, and J. T. Conroy, by the evaporation of a soln. of ferrous sulphate in an excess of sulphuric acid at  $60^\circ$  to  $80^\circ$ . R. de Forcrand could not confirm the existence of the trihydrate. W. Stortenbeker said that ferrous sulphate forms solid soln. with tritaoctohydrated cadmium sulphate, so that the **tritaoctohydrate**,  $3\text{FeSO}_4 \cdot 8\text{H}_2\text{O}$ , exists only in the isomorphous admixture.

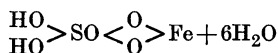
P. A. von Bonsdorff said that when sulphuric acid is slowly added to a sat. soln. of ferrous sulphate, so as not to produce any marked rise of temp., until the sp. gr. is 1.33, and the soln. is evaporated over conc. sulphuric acid, crystals of the heptahydrate appear; and when about two-thirds of the liquid has evaporated, crystals of the tetrahydrate are deposited; then follows a crop of crystals of a basic sulphate; and finally, a dark green, crystalline mass of the **dihydrate**,  $\text{FeSO}_4 \cdot 2\text{H}_2\text{O}$ , is formed. V. Schemlyanitzuin and N. Dobrovolsky obtained the dihydrate in a vat of copperas. T. Bolas, and J. B. Hannay obtained the dihydrate by the dehydration of the heptahydrate by sulphuric acid; T. E. Thorpe and J. I. Watts, by repeated treatment of the heptahydrate with boiling absolute alcohol; J. T. Conroy, by the action of sulphuric acid on the tetrahydrate; A. Étard, by heating the aq. soln. at temp. up to  $160^\circ$ ; and J. B. Hannay, by heating the heptahydrate, when the dihydrate shows itself as a break in the dehydration curve at  $100^\circ$ . According to F. K. Cameron, the dihydrate appears as a stable phase in contact with its sat. soln. above  $67.4^\circ$  under conditions where F. Fränckel, and others said that the solid phase is the monohydrate. F. K. Cameron also added that the dihydrate is stable at  $65^\circ$  in contact with aq. soln. containing over 2.5 per cent. of sulphuric acid; and he obtained it as a finely-divided, white, crystalline powder which is quite stable in dry air, and which dissolves in water more slowly than the other hydrates.

E. Mitscherlich observed that when the heptahydrate is heated to  $140^\circ$ , in vacuo, the **monohydrate**,  $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ , is formed, and it persistently retains the odd mol. of water up to between  $200^\circ$  and  $300^\circ$ . K. Klüss obtained the monohydrate by heating the heptahydrate at  $200^\circ$ . G. Keppeler and J. d'Ans poured a feebly acidic soln. of ferrous sulphate into alcohol, and heated the product dried by suction, in a current of hydrogen at  $70^\circ$ , and finally at  $150^\circ$  to  $200^\circ$ . The conditions of stability in aq. soln. are, according to F. Fränckel, indicated in Fig. 640, so that it is considered to be the stable phase in soln. containing 35.57 to 27.15 per cent.  $\text{FeSO}_4$  at temp. between  $64.0^\circ$  and  $90.13^\circ$ . F. K. Cameron said that the monohydrate is here mistaken for the dihydrate—*cf.* Fig. 640. W. Müller-Erbach demonstrated the existence of this hydrate from its effect on the vap. press. curve. F. B. Kenrick observed the monohydrate to be the stable phase in the system:  $\text{FeSO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$  in soln. with a mol of  $\text{SO}_3$  in 2.186 to 7.93 mols of water.

F. Wirth showed that the transition temp. :  $\text{FeSO}_4 \cdot 7\text{H}_2\text{SO}_4 \rightleftharpoons \text{FeSO}_4 \cdot \text{H}_2\text{O} + 6\text{H}_2\text{O}$ , is lowered about  $25^\circ$  by sulphuric acid, and he obtained the monohydrate by bringing the heptahydrate in contact with a soln. of concentration exceeding  $12.5N\text{-H}_2\text{SO}_4$ . D. Link, R. Scharizer, F. Jeremin, A. Étard, H. Lescœur, and A. Scott obtained it by adding conc. sulphuric acid to a sat. soln. of ferrous sulphate. R. Scharizer obtained the monohydrate by allowing the heptahydrate to effloresce for a long period in dry air; and J. B. Hannay, and E. Moles and M. Crespi, by passing air dried by sulphuric acid over the heptahydrate at  $100^\circ$ . R. Scharizer reported the monohydrate to occur with römerite near Copiapo, Chile, and he called it **ferropallidite**. It was previously observed by J. B. Macintosh. The mineral was also called *szomolnokite*—after Szomolnok, Hungary—and *schmölnitzite*. D. Florentin said that the monohydrate can be prepared in the following manner; and added that the product is non-hygroscopic, and undergoes no change when kept for long periods, so that it is suitable for use in standardizing such soln. as potassium permanganate, etc.

Dissolve in 200 c.c. of 50 per cent. sulphuric acid, assisted by warming on a water-bath, 400 grms. of ferrous sulphate, purified by re-crystallization several times. Almost as soon as solution is complete, the monohydrate begins to separate as a colourless crystalline powder, which is collected on a suction filter, washed with alcohol or dry acetone, then with dry ether, and finally dried by reduced press. over sulphuric acid. The yield is about 40 grms.

T. Graham, E. Mitscherlich, H. Precht and K. Kraut, J. B. Hannay, T. E. Thorpe and J. I. Watts, G. Keppeler and J. d'Ans, W. Peters, A. Rosentiehl, etc., observed that the heptahydrate gives off six-sevenths of its water at a comparatively low temp., say  $115^\circ$ , but the remainder is not given off until a much higher temp. is attained, say  $280^\circ$ . T. Graham thought that this odd molecule can be expelled without the loss of acid, but R. de Forcrand observed that if the dehydration temp. exceeds  $140^\circ$ , in vacuo, the anhydrous salt is always contaminated with some basic salt. R. Scharizer observed that 3 of the mols. of water are evolved fairly quickly over sulphuric acid in a desiccator, but the other 3 mols. occupy a long time—many months indeed. The first 3 mols. pass off at  $40^\circ$ , and the next 3 mols. at about  $70^\circ$ , but the remaining mol. is retained very tenaciously. T. Graham designated the odd mol. of water, *constitutional water*; J. von Liebig, *Halbhydratwasser*. T. Graham wrote  $\text{HO} \cdot \text{Fe} \cdot \text{HSO}_4 + 6\text{H}_2\text{O}$  as the formula for the heptahydrate, and this agrees with the opinions of W. Müller-Erbach, R. Scharizer, and D. Florentin. W. T. Schaller wrote the formula :



and A. Werner,  $[\text{Fe}(\text{H}_2\text{O})_6\text{SO}_4] \cdot \text{H}_2\text{O}$ . R. Reinicke discussed the spatial arrangement on the assumption that the 6 mols. of water are arranged about the six corners of an octahedron model. In connection with T. Graham's view that the monohydrate is constituted as if it were **ferrous hydroxyhydrosulphate**,  $\text{Fe}(\text{OH})(\text{HSO}_4)$ , it is interesting to observe that F. B. Kenrick prepared the acidic salt, **ferrous hydrosulphate**,  $\text{Fe}(\text{HSO}_4)_2$ , i.e. P. A. von Bonsdorff's  $\text{FeSO}_4 \cdot \text{H}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ . This is in accord with C. S. Mummery's theory of the catalytic action of ferrous sulphate on hydrogen dioxide, etc.

**The physical properties of ferrous sulphate.**—Melanterite occurs massive and pulverulent; but usually in capillary, fibrous, stalactitic, or concretionary forms; its colour is green of various shades, and in the case of thin fibres, or of pulverulent forms, it is almost white. When it has been exposed to the air, it becomes yellowish. A. Bussy and L. R. Lecanu, and C. Hensgen said that the anhydrous sulphate is white, and E. Greulich added that when 1.9 per cent. of ferric sulphate is present, the colour is greyish-white. E. Jordis and H. Vierling, J. S. Anderson, and N. A. Tananaeff said the crystals of the heptahydrate are blue or bluish-green;

and A. Piccini and F. M. Zuco, green. A. P. von Bonsdorff observed that the crystals are blue with a green tinge if free from ferric salt, but if a ferric salt is present the green colour predominates. M. Bamberger and R. Grengg added that the pale green crystals of the heptahydrate become greenish-white when cooled to  $-190^{\circ}$ . C. Hensgen said that the crystals of the hexahydrate are bright green; L. de Boisbaudran, and J. C. G. de Marignac, that the crystals of the pentahydrate are bluish-green or greenish-blue; P. A. von Bonsdorff, that the crystals of the tetrahydrate are chrysoprase green, pale green, or pale apple-green, without a blue tinge; R. J. Kane, that the crystals of the trihydrate are a much paler green than those of the heptahydrate; P. A. von Bonsdorff, that the crystals of the dihydrate are dark green; and W. Peters described the crystals of the monohydrate as pale yellowish-brown. A. Étard said dirty white, F. Jeremin, and D. Florentin, white. The general result is to show that the heptahydrate is pale greenish-blue, and that the colour weakens as the proportion of water diminishes until the monohydrate appears when it and the anhydrous salt are colourless or white. J. S. Anderson, and T. Dreisch said that dil. aq. soln. with a mol of salt per litre are nearly colourless; but more conc. soln. are pale green. N. A. Tananaeff observed that the pale blue crystals form a colourless soln. which becomes green by oxidation, and later brownish-yellow. R. Peters added that the soln. in contact with a platinum electrode charged with hydrogen, is colourless in thin layers, and pale green in layers of 1 mm. thickness.

T. Bolas said that the anhydrous sulphate furnishes white, microscopic, prismatic **crystals**. According to P. Groth, the crystals of the heptahydrate are monoclinic prisms probably with a pseudorhombohedral structure. V. R. von Zepharovich gave for the axial ratios  $a : b : c = 1.1828 : 1 : 1.5427$ , and  $\beta = 104^{\circ} 15' 5''$ ; and W. T. Schaller,  $1.1828 : 1 : 1.5421$ ; and  $\beta = 104^{\circ} 14'$ . The crystals were examined by H. E. Armstrong and E. H. Rood, H. Baumhauer, T. Bergman, M. H. Hey, F. S. Beudant, I. Eques a Born, H. J. Brooke, L. J. M. Daubertin, C. von Hauer, R. J. Haiiy, R. Kirwan, F. Mohs, C. Pape, J. C. Poggendorff, C. F. Rammelsberg, G. Rose, J. B. L. Romé de l'Isle, J. G. Wallerius, W. H. Wollaston, and C. Wöllner. The **habit** of the crystals is in short columns or thick plates with well-developed basal surfaces; when grown in soln. containing copper sulphate, H. Baumhauer found that the crystals are pseudorhombohedral; and in soln. with alum, C. Wöllner said that the crystals are regular octahedra. F. S. Beudant observed the effect of sodium borate and phosphate, lead sulphate, and hydrochloric and sulphuric acids; H. Reinsch observed that the presence of nitric acid had no influence on the habit of the crystals. O. Mügge discussed the formation of capillary, curved crystals. R. O. Lehmann described the effect of rapid cooling of hot, sat. soln. in the crystallization; and D. Gernez, the crystallization of supersaturated soln. J. M. Thomson studied the seeding of supersaturated soln. of magnesium sulphate with heptahydrated ferrous sulphate. E. Küster observed the **rhythmic crystallization** of the salt in gelatine. A. Drevermann measured the **rate of crystallization**; and C. L. Wagner, the rate of dissolution of the crystals. G. Schendell said that the rate of crystallization is accelerated in an electric field; and R. Hunt, S. Meyer, and G. Roasio studied the effect of a magnetic field on the crystallization of the salt. The **cleavage** of the crystals of the heptahydrate is perfect on the (001)-faces, and indistinct on the (110)-face. R. Scharizer said that the (010)-cleavage of the tetrahydrate is perfect. The **optical character** of the crystals of the heptahydrate is positive; and A. des Cloizeaux found the **optic axial angles**  $2H_0 = 86^{\circ} 51'$ ,  $2H_0 = 94^{\circ} 13'$ , and  $2V_a = 86^{\circ} 21' 5''$  for red-light;  $2H_a = 86^{\circ} 49'$ ,  $2H_0 = 94^{\circ} 21'$ , and  $2V_a = 86^{\circ} 13'$  for yellow-light; and  $2H_a = 86^{\circ} 31'$ ,  $2H_0 = 94^{\circ} 46'$ , and  $2V_a = 85^{\circ} 53' 5''$  for blue-light. M. Eroféef gave  $2V = 85^{\circ} 31'$  for Li-light;  $85^{\circ} 27'$  for Na-light, and  $85^{\circ} 23'$  for blue-light. R. Scharizer found  $2V$  to be large for the tetrahydrate. The **corrosion figures** were studied by H. Baumhauer, and E. Blasius, and the etching of the crystals by efflorescence, by E. Blasius, C. Gaudefroy, and C. Pape. H. G. K. Westenbrink found that the

**X-radiograms** correspond with a space-lattice having  $a=15.34$  Å.,  $b=12.98$  Å., and  $c=20.02$  Å. for the elementary cell, and 16 mols.  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  per cell. A. Johnsen said that the X-radiograms show that the 7 oxygen atoms of the combined water are not symmetrically oriented in the molecule. E. Terlandy discussed the inner structure of the crystals.

Ferrous sulphate forms solid soln. and is probably **isomorphous** with the sulphates of copper, magnesium, zinc, cadmium, vanadium, chromium, manganese, iron, cobalt, and nickel—*vide infra*. G. Agde and H. Barkholt studied the solid soln. of copper and ferrous sulphates; and E. Dittler, overgrowths of the heptahydrate with that of cobalt sulphate. A. Carnot observed that manganese can replace iron in isomorphous admixture, as in the mineral *luckite*. V. R. von Zepharovich found that the crystals of heptahydrated ferrous sulphate are isomorphous with the corresponding salt of magnesium, and in the impure Swedish mineral, *botryogene*, of J. Blaas, and J. Hockauf, magnesium replaces part of the iron in solid soln.

V. R. von Zepharovich found that isomorphous admixtures with 20 per cent. of magnesium salt have the axial ratios,  $a:b:c=1.1814:1:1.5428$ , and  $\beta=104^\circ 19.5'$ ; and with 40 per cent. of magnesium salt,  $1.1799:1:1.5434$ , and  $\beta=104^\circ 26'$ —see Fig. 641. W. Stortenbeker's study of the solid soln. of the two salts is summarized in Fig. 641.

O. Lehmann described a different modification of the crystals of the heptahydrate which were produced by cooling a hot, acidified, aq. soln. of the heptahydrate. The crystals of the heptahydrate are **dimorphous**. E. Mitscherlich found that the crystals obtained by crystallization from a soln. of ferrous sulphate at  $80^\circ$ , or by boiling the crystals of the heptahydrate with alcohol, are probably rhombic, and W. Haidinger supposed the eight-sided prismatic crystals so obtained were hemi-heptahydrated. G. H. O. Volger, and J. A. Krenner established the existence of a labile, rhombic form of the heptahydrate, which occurs in nature as the mineral *tauriseite*—*vide supra*. The rhombic heptahydrate is said to be obtained from the aq. soln. at a temp. a little above  $0^\circ$ , and L. de Boisbaudran obtained it by seeding a soln. of the heptahydrate with a crystal of heptahydrated magnesium, zinc, or nickel sulphate. W. Stortenbeker said that the rhombic crystals are more soluble than the monoclinic form; and J. W. Retgers, that their sp. gr. is less. J. W. Retgers also observed that the crystals of the solid soln. with a high proportion of magnesium sulphate, are rhombic—Fig. 641.

L. de Boisbaudran found that the crystals of the hexahydrate are monoclinic, possibly isomorphous with the corresponding nickel salt; he could not prepare a tetragonal hexahydrate. J. C. G. de Marignac observed that the pentahydrate furnishes pinacoidal crystals belonging to the triclinic system. The crystals have the axial ratios,  $a:b:c=0.5962:1:0.5770$ , and  $\alpha=81^\circ 23'$ ,  $\beta=110^\circ 28'$ , and  $\gamma=105^\circ 33'$ , and they are isomorphous with the corresponding copper and manganese sulphates; L. de Boisbaudran studied the isomorphism of the crystals of the pentahydrate with those of the corresponding copper sulphate. E. Mitscherlich obtained prismatic crystals of the tetrahydrate, which, according to J. C. G. de Marignac, are monoclinic prisms with the axial ratios,  $a:b:c=0.4373:1:0.5833$ , and  $\beta=91^\circ 3'$ . R. Scharizer gave for the monoclinic crystals of the tetrahydrate,  $a:b:c=0.43797:1:0.58715$ , and  $\beta=89^\circ 29'$ . The (010)-cleavage is distinct. H. V. Regnault, and P. A. von Bonsdorff said that the crystals are isomorphous with the corresponding manganese salt. C. F. Rammelsberg described a rhombic modification of the tetrahydrate; and the subject was discussed by E. S. von

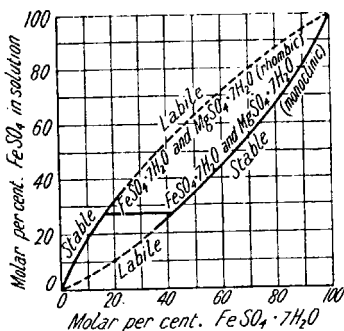


FIG. 641.—The Specific Gravities of Solid Solutions of Magnesium and Ferrous Sulphates.



Fedoroff, and P. Groth. W. Stortenbeker observed that the tritaoctohydrate exists only in isomorphous admixture with the monoclinic cadmium salt. R. Scharizer said that the monohydrate, ferropallidite, probably occurs in monoclinic crystals isomorphous with kieserite,  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ ; and J. A. Krenner gave the axial ratios,  $a : b : c = 0.9544 : 1 : 0.8999$ .

The **specific gravity** of anhydrous ferrous sulphate was found by E. Filhol to be 2.841, but this value is too low since L. Playfair and J. P. Joule gave 3.138, and 3.48 at  $4^\circ$ ; and T. E. Thorpe and J. I. Watts, 3.346 at  $15^\circ$ —the best representative value is 3.30. The sp. gr. of the monoclinic crystals of the heptahydrate was determined by P. van Muschenbroek, E. Günther, and many others. R. Boyle gave 1.88; L. Playfair and J. P. Joule, 1.857, and at  $4^\circ$ , 1.8889; E. Filhol, 1.904; H. Schiff, 1.884; H. J. Buignet, 1.902; S. Holker, 1.851 at  $15.5^\circ$ ; C. Pape, 1.9854 at  $16^\circ$ ; J. W. Retgers, 1.898 at  $18^\circ/4^\circ$ , and 1.899 at  $15^\circ/4^\circ$ ; H. G. F. Schröder, 1.881 to 1.897; F. Fränckel, and R. Scharizer, 1.89; W. C. Smith, 1.896; J. L. Andrae, 1.8988 at  $11.4^\circ/4^\circ$ ; 1.8989 at  $15.1^\circ/4^\circ$ ; and 1.8959 at  $37.6^\circ/4^\circ$ ; and E. Moles and M. Crespi, 1.895 at  $25^\circ/4^\circ$ . L. Michel gave 1.95 for the sp. gr. of melanterite, and J. Janowsky, 1.79. J. W. Retgers calculated the sp. gr. of the rhombic form of the heptahydrate to be 1.875 by extrapolation from observations on the solid soln. with magnesium sulphate, Fig. 641. E. S. Larsen gave 2.2 for the sp. gr. of the pentahydrate. T. E. Thorpe and J. I. Watts found the sp. gr. of the tetrahydrate to be 2.227 at  $15^\circ$ ; R. Scharizer, 2.2775; E. Moles and M. Crespi, 2.293 at  $25^\circ/4^\circ$ ; and F. Fränckel, 2.277. C. Pape found the sp. gr. of the trihydrate to be 2.268 at  $16^\circ$ ; and T. E. Thorpe and J. I. Watts gave 2.773 at  $15^\circ$  for the sp. gr. of the dihydrate. L. Playfair and J. P. Joule gave 3.047 for the sp. gr. of the monohydrate; E. Moles and M. Crespi, 2.970 at  $25^\circ/4^\circ$ ; and for ferropallidite, J. Donau, and R. Scharizer gave 3.083 at  $20^\circ$ ; and J. A. Krenner, 3.034. The **molecular volume** of the anhydrous salt was estimated by T. E. Thorpe and J. I. Watts; H. H. Stephenson gave 48.5; and 147.5 for the heptahydrate. Estimates were also made by F. Ephraim and P. Wagner, and T. E. Thorpe and J. I. Watts. H. Schiff estimated that a gram of the water of crystallization in the heptahydrate occupies 0.72 c.c.; and E. Moles and M. Crespi estimated that the mol. vol. of each of the first 3 mols. of water lost by the heptahydrate is 16.3, and of the next 3, 13.4. H. G. K. Westernbrink calculated the ratio—volume of unit cell : the number of contained molecules to be 241.4  $\text{\AA}^3$ . The **molecular contraction** which occurs when the anhydrous salt is formed from its elements was calculated by H. H. Stephenson, I. I. Saslawsky, N. Schiloff and L. Lepin, and J. N. Rakshit; for the heptahydrate, by L. de Boisbaudran, J. J. Saslawsky, J. N. Rakshit, and A. Balandin; and for the tetrahydrate, dihydrate, and monohydrate, by J. N. Rakshit.

Observations on the sp. gr. of aq. soln. of ferrous sulphate were made by G. Agde and H. Barkholt, P. Barbier and L. Roux, F. Flöttmann, G. Charpy, A. Heydweiller, E. Klein, J. Königsberger, J. G. MacGregor, W. Manchot and co-workers, W. W. J. Nicol, G. Quincke, A. Hauke, G. Piaggese, H. Schiff, H. Sentis, C. Tissier, J. Thomsen, and I. Traube. G. T. Gerlach gave for the sp. gr. of soln. with the following percentage proportions of the heptahydrate, at  $15^\circ$ :

$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ .	1	5	10	15	20	25	30	35	40 per cent.
Sp. gr..	1.005	1.0267	1.0537	1.0823	1.1124	1.1430	1.1738	1.2063	1.2391

and for soln. with the following proportions of the anhydrous salt, at  $18^\circ/4^\circ$ :

$\text{FeSO}_4$ .	0.1386	0.1708	0.2212	0.3614	0.5240	0.6921	0.8668	0.9878	per cent.
Sp. gr..	1.00000	1.000035	1.00091	1.00233	1.00388	1.00551	1.00791	1.00832	

E. Wiedemann discussed the vol. changes which occur when the soln. is heated. J. N. Rakshit gave for soln. with  $p$  per cent.  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , at  $10^\circ/20^\circ$  to  $60^\circ/20^\circ$ :

	$10^\circ$	$20^\circ$	$30^\circ$	$40^\circ$	$50^\circ$	$60^\circ$
Sp. gr. $\left\{ \begin{array}{l} p = 1^\circ \\ p = 5^\circ \\ p = 10^\circ \\ p = 20^\circ \end{array} \right.$	$\left\{ \begin{array}{l} 1.00780 \\ 1.02980 \\ 1.05900 \\ 1.11880 \end{array} \right.$	$\left\{ \begin{array}{l} 1.00600 \\ 1.02772 \\ 1.05620 \\ 1.11540 \end{array} \right.$	$\left\{ \begin{array}{l} 1.00330 \\ 1.02375 \\ 1.05200 \\ 1.1110 \end{array} \right.$	$\left\{ \begin{array}{l} 0.99980 \\ 1.02015 \\ 1.04828 \\ 1.10720 \end{array} \right.$	$\left\{ \begin{array}{l} — \\ 1.01620 \\ 1.04400 \\ 1.10300 \end{array} \right.$	$\left\{ \begin{array}{l} — \\ 1.01160 \\ 1.03936 \\ 1.09820 \end{array} \right.$

P. F. Gaehr represented the relation between the sp. gr.,  $D$ , and the percentage composition,  $C$ , by  $\log D = aC$ , where  $a$  is a constant. H. Schiff gave an interpolation formula for soln. with  $p$  per cent. of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , sp. gr.  $= 1 + 0.005175p + 0.043043p^2 - 0.07682p^3$  at  $17.2^\circ$ ; and J. G. MacGregor gave for the sp. gr. at  $20^\circ$ ,  $D = 0.99827 + 0.0099486p$ , where  $p$  denotes the per cent. of  $\text{FeSO}_4$ . The contraction which occurs when the heptahydrate is dissolved in water was studied by G. Charpy, I. Traube, L. Playfair and J. P. Joule, C. Tissier, R. Broom, H. Schiff, and G. T. Gerlach. J. N. Rakshit found for the contraction  $\delta v$  per mol. which occurs on dissolving  $p$  per cent. of the heptahydrate in water :

		10°	20°	30°	40°	50°	60°
$\delta v$	$p = 1^\circ$	34.3	35.1	19.7	5.3	—	—
	$p = 5^\circ$	19.8	19.6	11.7	4.5	3.8	4.3
	$p = 10^\circ$	20.4	18.0	13.3	10.2	8.9	8.9
	$p = 20^\circ$	16.3	14.3	11.7	10.1	9.7	9.4

E. Sonstadt observed that there is a contraction when crystals of the heptahydrate are added to a sat. soln. of ferrous sulphate, and this is attributed to adsorption. I. Traube discussed the molecular solution volume; A. Tafel, the temp. of maximum density; and H. Groshans, the density number.

The **hardness** of melanterite is said to be 2.0 on Mohs' scale. J. C. Graham found the coeff. of **diffusion** of 2 to 5 per cent. soln. of ferrous sulphate, in water at  $14^\circ$  to  $16^\circ$ , to be 0.338 per sq. cm. per day. Observations on the subject were also made by C. L. Wagner, R. E. Liesegang, and J. J. Coleman. J. Dewar found that when the heptahydrate is subjected to a high press., it exhibits **plastic flow**, as if it were a viscous fluid. Observations on the **surface tension** of aq. soln. were made by J. L. M. Poiseuille, H. Sentis, S. Oka, and C. Forch. The following observations on the surface tension,  $\sigma$  dynes per cm., and the **specific cohesion**,  $a^2$  per sq. mm., at  $15^\circ$  to  $18^\circ$ , are due to A. Brümmer, H. Stocker, and G. Meyer and H. Stocker. The soln. contain the percentage proportions of  $\text{FeSO}_4$  indicated. Those marked by an asterisk are by A. Brümmer, and the others, by H. Stocker, also contained 0.67 vol. per cent. of  $\text{H}_2\text{SO}_4$  :

$\text{FeSO}_4$	0.00	3.647*	7.181*	11.661*	15.62	17.906*
$\sigma$	72.52	68.67	67.36	69.34	74.75	76.55
$a^2$	145.24	132.60	125.73	123.80	128.04	128.54

C. Brunner could detect no evidence of any action by a magnetic field on the capillary ascent of the aq. soln. Z. H. Skraup studied the capillary movements in filter-paper; and J. G. F. Druce, and E. W. Washburn, the crawling of the soln. on the walls of the containing vessel.

L. Playfair and J. P. Joule gave 0.000072 for the coeff. of cubic **thermal expansion** of the heptahydrate; and J. L. Andreae, 0.000066 between  $14^\circ$  and  $38^\circ$ . E. Wiedemann added that the heptahydrate expands regularly up to its m.p.,  $65^\circ$ , and with further heating there is an abrupt expansion when the salt fuses. The thermal expansion of aq. soln. of the salt can be calculated from the data given above. C. H. Lees found the **thermal conductivity** of the heptahydrate to be 0.0013 to 0.0014 cal. per cm. per degree per second at  $15^\circ$ . C. Pape was unable to obtain satisfactory data for the **specific heat** of the anhydrous salt because it oxidized so readily when heated; for the heptahydrate, between  $25^\circ$  and  $100^\circ$ , he obtained 0.357 for the sp. ht.; H. Kopp gave 0.346 between  $18.5^\circ$  and  $46.5^\circ$ ; C. Forch and P. Nordmeyer, 0.239 between  $-190^\circ$  and  $14^\circ$ ; whilst F. G. Jackson obtained 0.292 between  $22^\circ$  and  $-78.4^\circ$ ; 0.234 between  $22^\circ$  and  $-190^\circ$ ; and 0.182 between  $-78.4^\circ$  and  $-190^\circ$ . L. Rolla and L. Accame found the molecular heat of the heptahydrate to be 92.147, between  $0^\circ$  and  $18^\circ$ , and of the tetrahydrate, 63.587, a difference of 28.56 for the loss of 3 mols. of water. C. Pape gave 0.247 for the sp. ht. of the trihydrate; but oxidation prevented him determining the sp. ht. of the monohydrate. J. Thomsen found the sp. ht. of a 4.1 per cent. soln.

to be 0.951 at 18°; and G. Agde and H. Holtmann found, between 25° and 45°, for soln. of the percentage composition :

FeSO <sub>4</sub> .	1	5	10	20	25	35	45	55	65 per cent.
Sp. ht. .	0.999	0.945	0.910	0.860	0.840	0.802	0.767	0.732	0.702

and the results for the ternary system, ferrous sulphate, sulphuric acid, and water between 25° and 45°, are summarized in Fig. 642.

E. Greulich represented the **thermal decomposition** of ferrous sulphate in the absence of air, by the equation:  $2\text{FeSO}_4 \rightleftharpoons \text{Fe}_2\text{O}_3 + \text{SO}_3 + \text{SO}_2$ , and J. d'Ans, and G. Keppeler and J. d'Ans supposed that this reaction progresses in two stages:  $6\text{FeSO}_4 \rightleftharpoons \text{Fe}_2(\text{SO}_4)_3 + 2\text{Fe}_2\text{O}_3 + 3\text{SO}_2$ ; and  $\text{Fe}_2(\text{SO}_4)_3 \rightleftharpoons \text{Fe}_2\text{O}_3 + 3\text{SO}_3$ ; or  $2\text{FeSO}_4 + 2\text{SO}_3 \rightleftharpoons \text{Fe}_2(\text{SO}_4)_3 + \text{SO}_2$ , or else, if a basic sulphate is formed,  $2\text{FeSO}_4 + \text{SO}_3 \rightleftharpoons \text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 + \text{SO}_2$ . The dissociation pressure,  $P$  cm., where  $P = p_{\text{SO}_3} + p_{\text{SO}_2} p_{\text{O}_2}$ , at different temp. is :

	235°	370°	482°	614.5°	645°	698°
$P$	0.1	2.0	7.3	25.4	58.7	126.3 cm.
$p_{\text{SO}_3}$	0.05	1.0	3.6	10.8	24.9	31.2 cm.
$p_{\text{SO}_2}$	0.05	1.0	3.7	13.8	32.0	82.3 cm.

The press. attains one atm. at 680°. The partial press. of the sulphur trioxide at  $T^\circ \text{K.}$  is  $\log p_{\text{SO}_3} = -2691.8T^{-1} + 5.1526$ . Observations on the partial press. of the sulphur dioxide and trioxide were made by G. Keppeler and J. d'Ans; the effect of water vapour and of ferrous oxide on the results was examined by J. d'Ans; and the effect of the formation of ferric sulphate on the results, by M. Bodenstein and T. Suzuki. J. A. Hedvall and J. Heuberger observed that in a current of nitrogen, the anhydrous sulphate suffers a perceptible decomposition at 510°. The thermal decomposition of the anhydrous salt was also studied by H. O. Hofman and W. Wanjukoff, G. Marchal, and B. Neumann. A. Bussy and L. R. Lecanu found that when heated in a retort with the partial exclusion of air, the anhydrous sulphate decomposes first, forming a basic sulphate:  $2\text{FeSO}_4 = \text{SO}_2 + \text{Fe}_2\text{O}_2(\text{SO}_4)$ , and finally ferric oxide. H. le Chatelier said that the decomposition begins at 700°; K. Honda and T. Ishiwara observed evidence of the decomposition at 560°; and R. H. Bradford observed no decomposition during

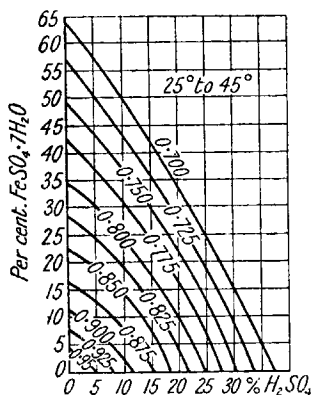


FIG. 642.—The Specific Heats of Aqueous Solutions of Ferrous Sulphate and Sulphuric Acid.

10 to 20 mins. at 500° to 585°; at 590°, the vapour of sulphur trioxide appears; and at 625° to 635°, 3 per cent. is decomposed in 2 hrs. K. Friedrich and co-workers said that the end-point of the decomposition agrees with the assumption that the ferric sulphate was the last to decompose. J. d'Ans observed that in an unlimited supply of air, anhydrous ferrous sulphate begins to oxidize perceptibly about 245°, and at 440°, the reaction is rapid; and G. Keppeler added that the thoroughly-dried anhydrous sulphate decomposes rapidly at 300°. Observations were also made by E. Kothny, R. H. Bradford, A. Nemes, P. Truchot, and E. F. Kern and W. H. Walter. The thermal decomposition of anhydrous ferrous sulphate in a current of dry air was found by W. S. Landis to be first evident at 550°; the rate of decomposition is but slight at 580°; it suddenly increases rapidly at 600°, so that the reaction ceases in

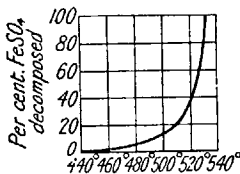


FIG. 643.—The Thermal Decomposition of Anhydrous Ferrous Sulphate in Air.

about 2 hrs., and very little more decomposition occurs until the temp. is raised to 960°. H. Saito said the decomposition begins at 550°. F. Warlimont represented the reaction in a current of air by the equation :  $6\text{FeSO}_4 + 3\text{O} = 2\text{Fe}_2(\text{SO}_4)_3 + \text{Fe}_2\text{O}_3$ . The percentage decomposition in 3 hrs., at different temp., Fig. 643, was :

	460°	475°	500°	510°	520°	530°	550°
Decomposition .	Trace	3	12	20	40	80	100 per cent.

H. H. Willard and R. D. Fowler discussed the separation of the metals by the differences in the rates of the thermal decomposition of their sulphates.

P. A. von Bonsdorff observed that the crystals of the heptahydrate effloresce in air to form a white powder. F. Fränckel found that the heptahydrate obtained by adding alcohol to a sat. soln. of ferrous sulphate loses some water in a few hours, but R. de Forcrand found the loss at 15° was negligible with the powdered salt. R. de Forcrand observed that the tetrahydrate did not effloresce in air at 15°, but it does so over conc. sulphuric acid; and R. de Forcrand, and D. Florentin found that the monohydrate does not effloresce in air, that it is non-hygroscopic in air, and does not oxidize in air. R. Scharizer found that the first 3 mols. of water are lost from the heptahydrate in 24 hrs. to 3 weeks, dependent on the grain-size of the material; 3 other mols. are lost very slowly and the transformation into the monohydrate occupies over a year. J. B. Macintosh also noticed that melanterite passes into the monohydrate on exposure to air, and that the change is accompanied by some oxidation. W. Müller-Erzbach observed that over conc. sulphuric acid, at 14° to 22°, the heptahydrate loses 3 to 4 mols. of water; and R. de Forcrand obtained the tetrahydrate in this manner after 3 days' exposure at 15°; R. Scharizer added that the monohydrate is formed after 13 weeks' exposure. J. F. Liverseege observed that when the heptahydrate was heated in a water-oven for 90 minutes, it left a residue containing 82.5 per cent. of  $\text{FeSO}_4$ , and 1 per cent. insoluble in water. J. Pritzker and R. Jungkunz found that 6 mols. of water are removed when the heptahydrate is heated in xylene. T. Graham observed that in vacuo, over phosphorus pentoxide, the heptahydrate lost 5.48 mols.; and in the high vacuum of the cathode light, over phosphorus pentoxide, F. Krafft, and A. Adolphi observed a loss of nearly 6 mols. of water. R. Scharizer studied the rate of dehydration of the heptahydrate over conc. sulphuric acid, and unlike the case with many other hydrated sulphates, no period of induction was observed. Measurements of the **vapour pressure** of the heptahydrate were made by W. Müller-Erzbach, H. Precht and K. Kraut, R. E. Wilson, and A. H. Pareau. E. Cohen and A. W. Wisser gave for the vap. press.,  $p$  mm. :

	30.67°	39.96°	44.45°	46.43°
$p$ . . . .	21.76	39.94	52.86	59.63 mm.

and W. C. Schumb observed that the heptahydrate passes into the hexahydrate when  $p$  at 25° is 14.56 mm. E. Wiedemann made observations on this subject.

C. Pape found that the heptahydrate shows signs of dehydration at 33°, and C. Gaudefroy, at 35°; but J. L. Andreae said that no water is lost by the crystals in benzene or in methylene or ethylene iodide at 37.6°. T. Graham observed that 6 mols. of water are lost at about 115°; H. Precht and K. Kraut, in vacuo at 79°; J. B. Hannay, at 100° in air dried by sulphuric acid; E. Moles and M. Crespi, in dry air at 100° to 120°; R. de Forcrand, in hydrogen at 100°; W. Peters, in hydrogen at 115°; T. E. Thorpe and J. I. Watts, in hydrogen at 120°; A. Rosenstiehl, in hydrogen at 140°; and G. Keppeler and J. d'Ans, in hydrogen at 150° to 200°. As indicated above, the seventh mol. of water was shown by J. J. Berzelius, R. Brandes, and T. Graham to be retained rather tenaciously; E. Mitscherlich said that in air it is lost above 200°; T. Graham, above 280°; A. Ditté, and A. Adolphi, at 280° to 300°; and E. Greulich, in hydrogen at 300°. In air or hydrogen, dried by phosphorus pentoxide, J. B. Hannay said that a part of the seventh mol. proportion of water is expelled at 100°, and T. E. Thorpe and J. I. Watts, and H. Precht and K. Kraut, said that all is expelled. In the high

vacuum of the cathode light, in the presence of barium oxide, F. Krafft, and A. Adolphi found that the last mol. of water is expelled. According to J. Waltl, at higher temp., the heptahydrate decomposes with the loss of sulphur trioxide to form a basic ferric sulphate, not the normal sulphate. H. O. Hofman and W. Wanjukoff found that when heated in an open tube in dry air, 3 mols. of water are lost between 20° and 72°; another 3 mols. between 80° and 123°; between 132° and 142°, a transformation occurs; between 150° and 366°, slow oxidation

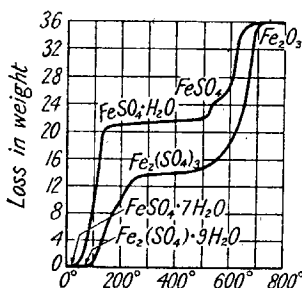


FIG. 644.—Heating Curves of Hydrated Ferrous and Ferric Sulphates.

occurs forming a basic ferric sulphate without loss of water; and between 406° and 482°, the last mol. of water is expelled, and  $\text{Fe}_2\text{O}_2\text{SO}_4$  is formed. E. Moles and M. Crespi found that the first 3 mols. of water are expelled at 60° to 70°, and the next 3 mols. at 100° to 120°. R. Scharizer said that in dry air, 3 mols. of water are lost at 40°; at 60° to 80° another 3 mols. of water are expelled, and oxidation sets in, and at 100° the sulphate is oxidized to a pale yellowish-brown powder; between 100° and 160°, the material retains two-sixths, and between 160° and 300°, one-sixth of a mol. of water. The remaining half mol. of water requires a red-heat for its expulsion. H. Saito's heating curve, obtained with a thermo-balance, is indicated in Fig. 644. J. B. Hannay obtained a heating curve showing breaks corresponding with the di- and mono-hydrates. Observations were also made by K. Honda and T. Ishiware, L. Hackspill and A. P. Kieffer, M. Copisarow, K. Friedrich and A. Blickle, and K. Friedrich. E. Beutel and A. Kutzelnigg found that the heptahydrate effloresces 5.14 times as fast when illuminated by ultra-violet light, and loses 3 mols. of water in 2 hrs.

W. W. J. Nicol, and W. Müller-Erbach measured the vap. press. of aq. soln. of ferrous sulphate, and for a sat. soln., at 65°, 75°, 85°, and 95°, the former gave  $p=165.7$ , 259.3, and 587.8 mm. respectively. G. Tammann observed that the **lowering of the vapour pressure** of water,  $\delta p$  mm., with soln. containing  $w$  grms. of  $\text{FeSO}_4$  per 100 grms. of water, is:

$w$ . . . . .	8.73	15.96	23.99	28.39	46.96	53.27
$\delta p$ . . . . .	6.6	11.0	16.5	20.3	43.7	49.8

G. Weidemann found that the crystals of the heptahydrate become white at about 73°, they sinter together at about 80°, and melt at about 90°. E. Wiedemann added that at the **melting-point** of the heptahydrate, the liquefaction is only partial, for the salt is more or less transformed into a lower hydrate; W. A. Tilden found that the break in the solubility curve at 64° corresponds with the m.p. of the heptahydrate. The **lowering of the freezing-point** of aq. soln. by ferrous sulphate was observed by C. Blagden, L. C. de Coppet, F. M. Raoult, N. Sasaki, N. Tarugi and W. Manchot, G. Bombardini, L. Kahlenberg, and F. Fränckel. W. Kistiakowsky found that with soln. containing 0.977, 1.458, 2.83, and 5.63 grms. of  $\text{FeSO}_4$  in 100 grms. of water, the f.p. were lowered respectively 0.15°, 0.23°, 0.415°, and 0.725°; and the mol. lowering of the f.p. ranged from 1.036 to 1.268. R. de Forcrand estimated the **boiling-point** of the heptahydrate to be 118.3°, of the tetrahydrate, 118.5°, and of the monohydrate, 300°. G. T. Gerlach found the b.p. of soln. with 17.7, 34.4, 50.4, and 53.4 grms. of  $\text{FeSO}_4$  per 100 grms. of water to be respectively 100.5°, 101.0°, 101.5°, and 101.6°. Observations on the **raising of the boiling-point** were made by W. W. J. Nicol, and N. Tarugi and G. Bombardini. L. Kahlenberg found that with soln. containing 3.245, 15.810, 26.645, and 35.35 grms. of  $\text{FeSO}_4$  per 100 grms. of water, the raisings of the b.p. were respectively 0.093°, 0.412°, 0.713°, and 1.099°.

E. Greulich calculated 189.5 Cals. for the **heat of formation** of anhydrous

ferrous sulphate between  $316^{\circ}$  and  $514^{\circ}$ . J. Thomsen gave for the heat of formation of the solid heptahydrate,  $(\text{Fe}, \text{O}_2, \text{SO}_2, 7\text{H}_2\text{O}) = 169.04$  Cals.; and in aq. soln.,  $(\text{Fe}, 4\text{O}, \text{S}, \text{Aq.}) = 236.283$  Cals.;  $(\text{Fe}, \text{O}, \text{SO}_3, \text{Aq.}) = 93.2$  Cals.;  $(\text{Fe}, \text{H}_2\text{SO}_4, \text{Aq.}) = 24.84$  Cals. with the escape of  $\text{H}_2$  gas;  $(\text{Fe}(\text{OH})_2, \text{H}_2\text{SO}_4, \text{Aq.}) = 24.92$  Cals. For the heat of formation in dil. soln., E. Greulich gave 234.9 Cals. R. de Forcrand gave  $\text{FeSO}_4 \cdot 4\text{H}_2\text{O} + 3\text{H}_2\text{O} = \text{FeSO}_4 \cdot 7\text{H}_2\text{O}_{\text{solid}}$ , 34.902, 5.922, and 1.632 Cals. according as gaseous, liquid, or solid water is assumed in the calculation; likewise for the solid tetrahydrate,  $\text{FeSO}_4 \cdot \text{H}_2\text{O} + 3\text{H}_2\text{O} = \text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ , 34.92, 5.939, and 1.650 Cals. according as gaseous, liquid, or solid water enters into reaction; similarly for the solid monohydrate,  $\text{FeSO}_4 + \text{H}_2\text{O} = \text{FeSO}_4 \cdot \text{H}_2\text{O}$ , 17.023, 7.363, and 5.933 according as gaseous, liquid, or solid water enters into the reaction. He observed no thermochemical grounds for assuming the existence of the di-, tri-, penta-, or hexa-hydrates. E. Cohen and A. W. Visser calculated 1.912 Cals. per mol. of water for the heat of transformation of the tetrahydrate into the heptahydrate. Observations were also made by P. A. Favre and J. T. Silbermann, and W. P. Jorissen. J. Thomsen gave for the **heat of neutralization** of a soln. of ferrous sulphate with potassium hydroxide,  $\text{FeSO}_4 + 2\text{KOH} = \text{K}_2\text{SO}_4 + \text{Fe}(\text{OH})_2 + 6.34$  Cals.; and with a soln. of barium hydroxide, 12.084 Cals. J. Thomsen gave  $-4.51$  Cals. for the **heat of solution** of a gram of the heptahydrate in 400 grms. of water; P. A. Favre and C. A. Valson gave  $-4.364$  Cals.; R. de Forcrand gave  $-4.323$  Cals. for the heat of soln. of the heptahydrate; 1.599 Cals. for the tetrahydrate; and 7.538 Cals. for the monohydrate. Observations were also made by P. A. Favre and J. T. Silbermann, and T. Graham. E. Greulich calculated 12.3 Cals. for the **heat of dissociation** of anhydrous ferrous sulphate between  $316^{\circ}$  and  $554^{\circ}$ ; and values were also calculated by G. Keppeler and J. d'Ans, and J. d'Ans:  $2\text{FeSO}_4 = (\text{Fe}_2\text{O}_3 + \text{SO}_3) + \text{SO}_2 + 6.1$  Cals. H. Schottky calculated values for the total and **free energy**,  $F$ , involved in the union of a mol. of ice with the hexahydrate to form the heptahydrate, and found  $F = 275$  cals., and the heat of combination  $Q = 200$  cals.

A. des Cloizeaux gave for the **index of refraction** of the crystals of the heptahydrate: 1.469 for red-light, 1.470 for yellow-light, and 1.478 for blue-light. M. Eroféef gave  $\alpha = 1.4681$ ,  $\beta = 1.4748$ , and  $\gamma = 1.4824$  for Li-light;  $\alpha = 1.4713$ ,  $\beta = 1.4782$ , and  $\gamma = 1.4856$  for Na-light; and  $\alpha = 1.4794$ ,  $\beta = 1.4861$ , and  $\gamma = 1.4928$  for blue-light. R. Scharizer gave  $\alpha = 1.533$ , and  $\beta = 1.535$  for the tetrahydrate. B. Wagner gave for the index of refraction,  $\mu$ , at  $17.5^{\circ}$ , of soln. containing per 100 c.c.

$\text{FeSO}_4$	1	2	4	6	8	10	12	15	20 grms.
$\mu$	1.33511	1.33696	1.34048	1.34393	1.34732	1.35064	1.35391	1.35871	1.36649

and A. Hauke found for a soln. with 12.74 per cent.  $\text{FeSO}_4$ , 1.3576 for the Na-line; 1.3595 for the Tl-line; and 1.3557 for the C-line. According to F. Flöttmann, the sp. gr. of 1 per cent. soln. of ferrous sulphate are respectively 1.0092, 1.0082, and 1.0070 at  $15^{\circ}$ ,  $20^{\circ}$ , and  $25^{\circ}$ ; and the indices of refraction for the D-line are respectively 1.33528, 1.33490, and 1.33443. Observations were also made by E. Doumer, E. E. Sundwik, F. Flöttmann, and B. Walter. For soln. with up to 34 per cent.  $\text{FeSO}_4$ , P. Bary observed a break in the concentration-refractive index curve corresponding with  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ . W. Sutherland calculated, with the  $\mu$ -formula, the molecular refraction of the heptahydrate 29.7 for the A-line; J. H. Gladstone and W. Hibbert gave 28.4. P. Barbier and L. Roux discussed the **dispersion** of soln. of different concentrations. P. Krishnamurti studied the **Raman effect**.

According to B. Franz, and R. Zsigmondy, soln. of ferrous sulphate, according to their concentration and thickness, absorb 90 to 98 per cent. of the **heat rays**. For **ultra-violet light**, *vide supra*. T. Dreisch observed with a 5 mm. layer of a soln. having 1 mol. of  $\text{FeSO}_4$  per litre, a strong maximum in the absorption band for light of wave-length  $\lambda = 0.95\mu$ , and a weak maximum for  $\lambda = 1.07\mu$ . H. M. Vernon discussed the change of the colour of soln. on dilution or on raising the temp. J. S. Anderson studied the **absorption spectrum** of the soln. and found for the

extinction coeff.,  $k$ , of soln. of a mol. of  $\text{FeSO}_4$  per litre, with layers between 0.14 and 2 cm. thick :

$\lambda$ . .	4340	4630	5470	6250	6870	7460	9000	11,750	13,000
$k$ . .	0.22	0.14	0.058	0.080	0.16	0.25	1.26	1.39	1.14

and for soln. with  $C$  mol of  $\text{FeSO}_4$  per litre :

$\lambda = 4530$					$\lambda = 6530$		
$C$ . . . .	1.5	0.75	0.5		1.5	0.75	0.5
$k$ . . . .	0.074	0.074	0.12		0.10	0.094	0.11

Observations were also made on the ultra-red visible rays by R. A. Houston, and R. A. Houston and C. Cochrane. A. Byk and H. Jaffe observed that the ultra-violet rays are also absorbed by soln. of ferrous sulphate, and that with increasing concentration, the absorption limits are displaced towards the longer wave-lengths. Thus, C. R. Crymble observed for 0.1*N*- and 0.01*N*-soln.,  $\lambda = 2580$  Å. for a 2 cm. layer, and  $\lambda = 2180$  Å. for a 1 cm. layer. Observations were also made by G. P. Drossbach, and S. Kato.

E. A. Owen found the mol. absorption coeff. of the anhydrous sulphate for the **X-rays**, 2369.5 for  $\lambda = 0.586$  Å., and 544.20 for  $\lambda = 0.35$  Å., when the value for water is 55.8. J. L. Glasson studied the absorption of X-rays by the heptahydrate; and W. Ackroyd and H. B. Knowles observed that heptahydrated ferrous sulphate is only a little less transparent for the X-rays than the corresponding salts of cobalt and nickel. The absorption coeff. of aq. soln. containing 1.08, 0.54, and 0.133 mol  $\text{FeSO}_4$  per litre were found by T. E. Aurén to be respectively 53.0, 56.5, and 58.4. Observations were also made by N. A. Schischakoff, and A. Hébert and G. Reynaud. According to H. Fricke and S. Morse, the rate of decomposition of 0.00878*M*- to 0.001*M*- $\text{FeSO}_4$  is linear for the same dosage of X-rays, but for increased dosages, the rate of decomposition is still linear, but the rate is halved. With a 0.000406*M*-soln. the rate of decomposition has a linear relationship to the X-ray dosage until decomposition is practically complete. With increased doses the conc. of ferrous sulphate is gradually restored to an equilibrium value about 50 per cent. of the initial one. In the first cases, the change in the rate of decomposition is shown to take place at the point where all the dissolved oxygen in the soln. has been used up. In the later stages of the decomposition, the transformation of the ferrous ions is a secondary effect due to activated water mols. produced by secondary X-ray electrons. The, apparent reversal of the reaction in the last case is attributed to the interference in the soln. of a reducing substance (perhaps hydrogen dioxide). N. A. Schischakoff, and G. L. Clark and L. W. Pickett studied the subject.

K. Niederstadt observed that the heptahydrate forms a pale green powder when exposed to **radium rays**; and A. Kailan studied the action of these rays on aq. soln. of the salt. E. Ohlon observed that at the temp. of liquid air, the heptahydrate does not luminesce when exposed to **cathode rays** or to **canal rays**; and it exhibits no **thermoluminescence** when warmed to room temp. E. Wiedemann and G. C. Schmidt found that the presence of ferrous sulphate weakens the **luminescence** of many substances, thus, 1 per cent. suppresses the **photoluminescence** of zinc sulphate; but W. Arnold found that the cathodoluminescence of lithium sulphate is strengthened by ferrous sulphate. A. E. Garrett observed that when heated to 360°, ferrous sulphate emits ions. W. Zimmermann observed the **photoelectric effect** of ferrous sulphate in ultra-violet light. H. Nisi studied the **Raman effect**. E. Giebe and A. Scheibe observed no **piezoelectric effect** with the heptahydrate. For the effect of an electric field on the crystallization of the salt, *vide supra*. The **magnetic rotatory power**, or **Verdet's constant**,  $\omega$ , for sat. soln. of ferrous sulphate, at 23°, in a field of about 12,050 gauss, for  $\lambda = 6000$  and 8000 Å., was found by L. R. Ingersoll to be respectively  $\omega = 0.0087$  and 0.0050. Observations were also made by M. E. Verdet, and O. Schönrock. F. Allison and E. J. Murphy

studied the magneto-optic properties; and W. Sucksmith, the gyromagnetic properties. The **magnetic dichroism** of soln. of ferrous sulphate in organic solvents was studied by G. Meslin. H. Hellmann and H. Zahn measured the **dielectric constant** of aq. soln. of ferrous sulphate.

E. Klein measured the **electrical conductivity** of aq. soln. of ferrous sulphate, at 18° and 26°. F. Kohlrausch and L. Holborn found the eq. conductivity,  $\lambda$ , and the sp. conductivity of soln. with a gram-equivalent of ferrous sulphate in  $v$  litres at 18°, and the temp. coeff.,  $\alpha$ , of the soln. between 18° and 22°, to be:

$v$	.	.	.	2	1	0.50	0.33	0.28
$\lambda$	.	.	.	30.8	25.8	19.5	15.37	13.21
Sp. cond.	.	.	.	154	258	390	461	470 mhos
$\alpha$	.	.	.	0.0218	0.0218	0.0223	0.0231	0.0243

L. Kahlenberg found similarly for the eq. conductivity,  $\lambda$ , and H. Vierling for the mol. conductivity,  $\mu$ , at 25°:

$v$	.	1	4	8	16	32	128	256	1024	2048
$\lambda$	{	16.3	23.0	28.1	31.4	36.3	47.2	52.1	59.5	62.0
	95°	60.6	89.2	103.5	125.5	104.2	211.5	250.3	319.9	413.1
$\mu$	.	—	56	84	96	118	165	189	264	300 (315)

where the number in brackets represents the value after 3 minutes, whereas the other number refers to a soln. one minute old. L. Kahlenberg also gave at 0°,  $\lambda=64.9$  for  $v=8192$ . W. Manchot gave  $\mu_{\infty}=230$  mhos. Observations on the conductivity of aq. soln. were also made by O. Mustad, F. Foerster, R. C. Wells, N. Tarugi and G. Bombardini, J. Trötsch, N. Sasaki, C. L. Wagner, and N. Sasaki. E. Klein found that the oxidation of the soln. by air has but little effect on the conductivity. H. Vierling examined the effect of hydrogen and oxygen in the presence and absence of platinum, and of sulphuric acid. F. Neesen observed that a magnetic field had no perceptible effect on the conductivity, and the subject was also studied by G. Berndt. The percentage **degree of ionization**,  $\alpha$ , of the soln. with a mol of the salt in  $v$  litres, at 18°, was found by W. Manchot to be:

$v$	.	15.6	33.3	80	160	640	1280	2560	5120
$\alpha$	.	38.5	45.9	54.6	66.1	80.7	87.0	97.6	97.6 per cent.

Observations were also made by N. Tarugi and G. Bombardini. The ionization factor,  $i=1.15, 10$ —was found by F. Fränkel for soln. with  $C$  grms. of  $\text{FeSO}_4$  per 100 grms. of water, at 0°:

$C$	.	.	.	1.0156	2.5974	5.1684	7.7369	13.483
$i$	.	.	.	1.39	1.17	1.03	1.00	0.984

Observations were also made by W. Manchot, W. Kistiakowsky, L. Kahlenberg, S. Arrhenius, and N. Tarugi and G. Bombardini. K. Szalagyi found the **transport number** of the  $\text{Fe}^{++}$ -ion to be 0.302 at 20°.

W. Manchot and co-workers calculated values for the **solvation or hydration** of the salt in aq. soln., i.e. the number of mols,  $n$ , of water bound up with a mol of  $\text{FeSO}_4$  at 25°, and obtained for soln. with 0.7256 and 1.4634 mols of  $\text{FeSO}_4$  per litre,  $n=26.7$  and 21.7 respectively. J. H. Walton and A. Brann studied the relation between the rate of crystallization and the degree of hydration of the molecules of the solute. According to J. H. Long, the **degree of hydrolysis** of 0.5N- $\text{FeSO}_4$  at 85° is 0.033 per cent. A. Krause found the **H<sup>+</sup>-ion concentration** of N- $\text{FeSO}_4$  to be  $p_{\text{H}}=3.5$ ; the electrometric titration for the determination of the acidity of the soln. was discussed by M. Koenig, B. Kamiensky, and T. Haczko. G. S. Tilley and O. C. Ralston said that hydrolysis begins with a H<sup>+</sup>-ion conc.  $10^{-9}$ , or a OH<sup>-</sup>-ion conc. of  $10^{-5}$ , but M. R. Thompson said that the ferrous salts begin to hydrolyze in a faintly acidic soln. with  $p_{\text{H}}$  probably 5 or 6, rather than in a faintly alkaline soln. with  $p_{\text{H}}=9$ , as suggested by G. S. Tilley and O. C. Ralston. P. A. von Bonsdorff found that a soln. free from ferric salts, and boiled with iron turnings does not affect the colour of blue-litmus, and only when the soln. is



oxidized by air does a blue coloration appear. C. C. Ahlum also found that the aq. soln. of ferrous sulphate is neutral to methyl orange. R. Saxon studied the electrolysis of soln. of the sulphate; and N. Kameyama and K. Takahashi, the electro-oxidation of the salt.

L. Riéty studied the potential of a soln. of ferrous sulphate flowing through a capillary tube under a press. of 25 atm. The **electromotive force** of various cells with a soln. of ferrous sulphate as one of the electrolytes was measured by J. A. Atanasiu and V. Stefanescu, W. D. Bancroft, B. Neumann, K. F. Ochs, and T. Swensson; M. Krieg studied the **polarization** of platinum in soln. of ferrous sulphate; and P. Baumann found the **decomposition voltage** of  $0.2N\text{-FeSO}_4$  to be 1.3 volts; and the subject was studied by H. Vierling. The electrolysis of soln. of ferrous sulphate from the point of view of the preparation of iron has been previously discussed. The anodic oxidation of the liquid during the electrolysis, and the deposition of hydrated ferric oxide was discussed by H. Buff, M. Berthelot, A. G. Betts, A. Brochet and J. Petit, A. Klemenc, J. H. Paterson, C. F. Schönbein, and Z. Karaoglanoff. According to M. M. Tichwinsky, when a 30 per cent. soln. of ferrous sulphate is electrolyzed between iron electrodes by a very weak current in the dark, a soln. is obtained in the course of a month or two which differs considerably from the ordinary soln. of ferrous salts. Its colour is more intensely green, somewhat like that of nickel sulphate, and on exposure to light, it deposits a green solid, which may be preserved for an indefinite period if air be excluded. Analysis of the soln. showed it to contain twice as much iron for a given quantity of sulphuric acid as is contained in ferrous sulphate. It therefore contains the basic salt, ferrous oxysulphate,  $\text{FeO}\cdot\text{FeSO}_4$ , which decomposes on exposure to light with the deposition of ferrous hydroxide which is coloured green by some ferrous sulphate carried down with it, and consequently the precipitate becomes paler in colour as it is washed. T. von Grotthus, and F. Braun studied the decomposition of an electrolyte in a narrow crack through which a current passes; F. Braun called the phenomenon electrostenolysis. It was also investigated by R. de Muynk. A. Schükareff observed that if the anode is in a magnetic field of 2000 to 7000 gauss during the electrolysis of a soln. of ferrous sulphate between platinum electrodes, the current between the plates is enhanced, but not so if the cathode be in the magnetic field.

M. Faraday observed that the paramagnetism of anhydrous ferrous sulphate is not perceptible at  $-45^\circ$ . The **magnetic susceptibility** of the solid was found by J. Königsberger to be  $\chi = 37 \times 10^{-6}$  mass unit at  $22^\circ$ ; G. Meslin gave  $\chi = 51 \times 10^{-6}$ ; and G. Berndt,  $\chi = 69.4 \times 10^{-6}$ . W. Finke gave for the three crystal axes, *a*, *b*, and *c*, respectively,  $84.32 \times 10^{-6}$ ,  $78.74 \times 10^{-6}$ , and  $76.20 \times 10^{-6}$ . With a field of about 2000 gauss, K. Honda and T. Ishiwara, and T. Ishiwara gave for the anhydrous salt:

	$-162.8^\circ$	$-56.3^\circ$	$8.5^\circ$	$88.0^\circ$	$286.3^\circ$	$404.3^\circ$	$642.3^\circ$
$\chi \times 10^6$	177.0	97.5	76.9	74.2	39.5	32.6	24.0

and H. K. Onnes and co-workers, with a field of 10,000 to 17,000 gauss, obtained:

	$-258.7^\circ$	$-253.0^\circ$	$-203.3^\circ$	$-202.7^\circ$	$-195.8^\circ$	$-103.5^\circ$	$17.1^\circ$
$\chi \times 10^6$	335	402	227.3	215.1	200.4	107.2	67.6

The results were found by H. K. Onnes and co-workers, T. Ishiwara, and K. Honda and T. Ishiwara to be in general agreement with the relation  $\chi(T + \theta) = \text{constant}$ —*vide supra*, the magnetism of iron. The effect of temp. on the magnetic susceptibility of the anhydrous salt was also studied by G. Foëx, and L. C. Jackson whose results for the reciprocal of the mol. magnetic susceptibility at different temp.,  $^\circ\text{K}$ ., are indicated in Fig. 645. W. Sucksmith studied the gyromagnetic effect.

The paramagnetism of the heptahydrate was studied by M. Faraday, T. J. Seebeck, and J. Plücker and A. Beer. C. B. Greiss observed some remanent magnetization, but C. Matteucci observed none. G. Berndt detected no hysteresis at

200 gauss. The behaviour of crystals of the heptahydrate when suspended in a magnetic field was studied by M. Faraday, J. Plücker and A. Beer, and H. E. Armstrong and E. H. Rodd. Observations on the magnetic susceptibility were made by J. Plücker, J. S. E. Townsend, G. Berndt, G. Meslin, L. C. Jackson, G. Falckenberg, M. H. Belz, S. Meyer, J. Königsberger, and G. Wiedemann. According to W. Finke, the vol. susceptibility of the heptahydrate in air, at 20°, in a field of 7800 gauss in the direction of the *a*-axis is  $84.32 \times 10^{-6}$ ; in the direction of the *b*-axis,  $78.74 \times 10^{-6}$ ; and in the direction of the *c*-axis,  $76.20 \times 10^{-6}$ . S. Meyer said that the magnetic susceptibility is independent of the field-strength between 600 and 10,000 gauss. K. Honda and T. Ishiware, and T. Ishiware gave for the susceptibility of the heptahydrate at different temp., and a field-strength of about 2000 gauss:

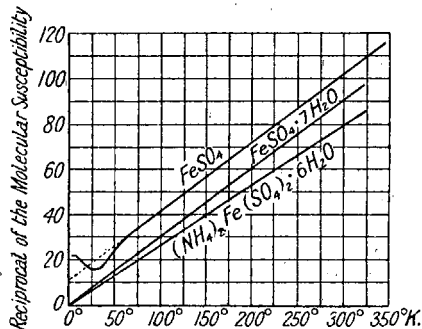


FIG. 645.—The Reciprocal of the Magnetic Susceptibility of Ferrous Sulphates.

	-173.6°	-109.7°	-53.5°	2.3°	103.7°	508.8°	930.9°
$\chi \times 10^6$	122.7	76.6	56.8	44.5	35.1	14.1	5.1

and H. K. Onnes and co-workers observed with a field-strength of 5000 to 14,000 gauss:

	-259.17°	-256.09°	-254.37°	-252.77°	-208.86°	-195.65°	16.5°
$\chi \times 10^6$	757.2	641.6	589.7	555.4	186.1	154.5	41.46

The relation  $\chi T$  ranges from 11,110 at  $-258.3^\circ$  to 12,390 at  $19.3^\circ$ . The subject was studied by E. Oosterhuis, C. A. Crommelin, and R. Gans. B. Cabrera and co-workers examined the influence of the water of hydration on the susceptibility of the salt.

M. Faraday studied the paramagnetism of the aq. soln. of ferrous sulphate. C. Matteucci observed no evidence of remanent magnetization. A. Quartaroli observed that a soln. with 3.17 grms. of Fe per litre is neutral with respect to magnetization for the paramagnetism of the salt then neutralizes the diamagnetism of the water. The changes in the form of the surface of the soln. in a magnetic field were studied by J. Plücker, J. Jamin, R. W. Roberts and co-workers, A. Quartaroli, W. Rathert, and A. Righi. Observations on the magnetism of the aq. soln. were made by A. Arndsten, E. Becquerel, I. Borgmann, H. W. Eaton, G. Heydweiller, J. Plücker, T. Wöhner, G. Wiedemann, and O. Wylach. G. Jäger and S. Meyer found the magnetic susceptibility,  $\chi$  mass unit, to be  $93 \times 10^{-6}$  at  $18^\circ$ ; J. S. E. Townsend gave  $75 \times 10^{-6}$  at  $10^\circ$ ; G. Quincke,  $82 \times 10^{-6}$  at  $19^\circ$ ; O. Liebknecht and A. P. Wills,  $84 \times 10^{-6}$  at  $18^\circ$ ; J. Königsberger,  $75 \times 10^{-6}$  at  $22^\circ$ ; G. Falkenberg,  $73.3 \times 10^{-6}$ ; and K. Honda and T. Ishiware,  $74.2 \times 10^{-6}$  at  $19.3^\circ$ . P. Weiss and C. A. Frankamp found for soln. of the following percentage composition, at  $12.6^\circ$  to  $18.6^\circ$ :

FeSO <sub>4</sub>	0.488	0.512	0.885	1.229	3.810	12.100	20.700
$\chi \times 10^6$	-0.3210	-0.3060	0.00141	0.2724	2.3580	9.0100	15.8700

The raising of the susceptibility of the heptahydrate as it passes into aq. soln. was observed by G. Wiedemann, and A. Heydweiller to be small; but J. Königsberger observed a very marked increase. G. Piaggese gave for the influence of temp. with the percentage concentration, *C*, and field-strength, *H*:

	<i>C</i> = 20.52; <i>H</i> = 3600			<i>C</i> = 12.95; <i>H</i> = 4100			<i>C</i> = 8.43; <i>H</i> = 7460		
	24.0°	69.5°	85.5°	16.6°	60.5°	86.8°	23.5°	61.3°	83.3°
$\chi \times 10^6$	24.275	23.077	20.203	12.525	11.207	10.401	6.812	6.478	5.770

The effect of temp. was also measured by E. Becquerel, H. Breternitz, P. Curie, G. Falckenberg, G. Jäger and S. Meyer, L. Lombardi, G. Meslin, P. Theodorides, A. E. Oxley, R. Oppermann, G. Piaggese, G. Quincke, P. Pascal, R. H. Weber, G. Wiedemann, and E. Wilson; the effect of concentration, by G. Falckenberg, G. Jäger and S. Meyer, J. Königsberger, R. Oppermann, A. Quartaroli, J. S. E. Townsend, and P. Weiss and C. A. Frankamp; the influence of the field-strength, by A. Arndtsen, G. Falckenberg, A. Heydweiller, G. Jäger and S. Meyer, J. Königsberger, L. Lombardi, P. Pascal, J. S. E. Townsend, T. Wähner, R. H. Weber, and O. Wylach; and the influence of changes in the frequency of the alternating current, by G. Falckenberg. The results were calculated to express mol. susceptibilities by A. Quartaroli, A. Heydweiller, O. Liebknecht and A. P. Wills, and P. Philipp; and the atomic susceptibilities, by P. Weiss and C. A. Frankamp, O. Liebknecht and A. P. Wills, and R. H. Weber. B. Cabrera and co-workers obtained for the mol. susceptibilities, at  $20\cdot3^\circ$ ,  $-195\cdot7^\circ$ , and  $-208\cdot4^\circ$  the respective values  $0\cdot011917$ ,  $0\cdot044612$ , and  $0\cdot053231$ ; and for Curie's relation,  $3\cdot498 = \chi(T+1\cdot1^\circ)$ . K. Honda and T. Ishiware calculated for the **magnetic moment** of anhydrous ferrous sulphate,  $4\cdot74 \times 10^{-20}$ ; whilst H. K. Onnes and E. Oosterhuis gave  $4\cdot72 \times 10^{-20}$ . R. Gans, and L. Pauling and M. L. Huggins calculated the **magneton number** of the heptahydrate to be  $26\cdot09$ ; and values for the salt in aq. soln. were calculated by B. Cabrera and co-workers, A. Quartaroli, R. H. Weber, P. Weiss, and P. Weiss and C. A. Frankamp. D. Samuracas found that the crystallization from aq. soln. is accelerated in a magnetic field.

**The chemical properties of ferrous sulphate.**—According to J. A. Arfvedson, anhydrous ferrous sulphate is reduced to iron disulphide when it is heated to redness in a current of **hydrogen**, and H. Rose observed that ferrous sulphide is formed. If the hydrogen is under a press. of 200 atm., W. Ipatéeff and A. Kisseleff found that ferrous sulphide, and microcrystalline ferrous oxide are formed, and at 260 atm., and  $350^\circ$ , only crystalline ferrous sulphide. At a high enough temp., the sulphate is reduced by hydrogen to metallic iron. G. Keppeler and J. d'Ans observed that the monohydrate passes into the anhydrous salt when heated at  $200^\circ$  in a current of hydrogen. S. Miyamoto found that the sulphate is reduced by hydrogen in the silent discharge. W. Ipatéeff and co-workers, and J. H. Weibel studied the reduction of ferrous sulphate in aq. soln. by hydrogen under press., and found that at  $330^\circ$  and 200 atm., ferrous sulphide and ferrous oxide are formed, whilst at  $350^\circ$  and 260 atm., crystalline ferrous sulphide alone is formed. For the reduction of ferric salts by nascent hydrogen, *vide infra*, the action of some metals on the soln. B. Neumann detected no reduction of the aq. soln. by hydrogen in the presence of platinum.

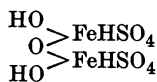
R. Brandes, and J. d'Ans observed that when the anhydrous salt is exposed to **air**, it readily takes up moisture, and in moist air, the heptahydrate is formed. The absorption of moisture is quicker if the ferrous sulphate is contaminated with ferric sulphate. The heptahydrate was found by P. A. von Bonsdorff to weather to a white powder on exposure to air—*vide supra*. At ordinary temp., the heptahydrate gradually acquires a brown colour on exposure to air at ordinary temp. owing to its oxidation to basic or normal ferric sulphate. The formation of a basic sulphate or sulphates was emphasized by A. Maus, R. Scharizer, and H. O. Hofman and W. Wanjukoff. The oxidation takes place more readily if the air be humid. R. Scharizer said that oxidation is of minor significance in dry air; but in moist air, the heptahydrate may liquefy in the adsorbed water, and oxidation proceeds apace. The imperfectly dried crystals also oxidize more rapidly than is the case if they have been thoroughly dried. Crystals which have been deposited from neutral soln. are more liable to aerial oxidation than crystals obtained from acidic soln. J. d'Ans, C. Baskerville and R. Stevenson, and F. Fränckel found that if the heptahydrate is of a high degree of purity, it is very much less readily oxidized in air, than is the case with the ordinary salt. P. Geiseler, and A. Piccini and F. M. Zuco observed that the crystals of the heptahydrate can be preserved

unchanged in a sealed tube for years. G. Welborn recommended the introduction of a few drops of ether in the tube before sealing; H. Hager, a little camphor wrapped up in paper; and A. Gawalowsky, a side tube containing a little alkaline soln. of pyrogallol and glass wool. H. Hager emphasized the need for completely removing the mother-liquor from the heptahydrate crystals; and R. de Forcrand recommended powdering the crystals, and repeatedly drying the powder by pressure between folds of filter-paper; he said that the product is quite stable in air at 15°. G. Ruspini discussed the preservation of the heptahydrate. P. Chastaing observed that the speed of oxidation of the powdered heptahydrate is increased by exposure to light, and that the red rays are more active than the violet. F. Thomas found that after exposing a soln. of ferrous sulphate to light and oxygen, the oxygen absorbed was relatively:

Red	Yellow	Green	Violet	Darkness
71	74	80	76	72

H. Fricke studied the influence of X-rays on the oxidation of aq. soln. of ferrous sulphate, and the results are independent of the wave-length.

R. Scharizer observed that in **oxygen**, the heptahydrate is readily oxidized to hygroscopic ferric sulphate; D. Tommasi also noted the tendency of the heptahydrate to oxidize in detonating gas. When the anhydrous salt is moderately heated in air, oxidation occurs, and the so-called *burnt or calcined green vitriol* is produced, and the product is considered to be a basic ferric sulphate,  $\text{Fe}_2\text{O}(\text{SO}_4)_2$ . The thermal decomposition of ferrous sulphate in a limited supply of air, and with the free access of air, has been previously discussed. The aq. soln. gradually becomes turbid on exposure to air, and a yellowish-brown basic salt is precipitated, and, according to F. Muck, the composition of the precipitate varies with the composition of the soln. This probably means that the basic salt is a hydrated ferric oxide with more or less adsorbed sulphate. R. Scharizer, and E. Manasse observed that if ferrous sulphate be warmed, oxidation is very rapid, and since, above 80°, all is present as monohydrate, it is assumed that the first stage of the oxidation involves the formation of the complex:



which breaks up into  $2\text{Fe}(\text{OH})\text{SO}_4$  and water; it is also supposed that a similar intermediate product is formed in the oxidation of aq. soln. of ferrous sulphate. W. Manchot and W. Pflaum, W. Franke, and H. Wieland and W. Franke discussed the formation of complexes in the oxidation of ferrous sulphate. T. Warynsky found that aq. soln. of ferrous sulphate are fairly stable provided the water be acidulated with dil. sulphuric acid; and A. Jilek observed no oxidation at the end of 48 hrs. with soln. containing sulphuric acid. Exposure to light accelerates the rate of oxidation, and F. Thomas found that with neutral soln., the relative rates of oxidation are: in red-light, 49; in yellow-light, 52; in green-light, 54; in violet-light, 53.5; and in darkness, 50, but the rate of oxidation of the acidified soln. was too slow for measurement under the conditions of these experiments. P. Chastaing, C. E. Nurnberger, and B. K. Mukerji and N. R. Dhar also compared the rate of oxidation of soln. of ferrous sulphate in light and in darkness. F. R. Ennos found that the rate of oxidation of the aq. soln. is proportional to the partial press. of the oxygen; and, according to C. G. MacArthur, the rate is reduced by the addition of conc. soln. of inert, soluble salts—*e.g.*, the chlorides and sulphates of sodium, potassium, or magnesium—whose presence decreases the solubility of oxygen. The oxidation is said to depend on the non-ionized portion of the dissolved salt. The relative rates of oxidation of chloride, sulphate, and acetate are as 1:10:100. The marked slowness of the oxidation of acidified soln. of ferrous sulphate was emphasized by C. Baskerville and R. Stevenson, who found

that no appreciable oxidation occurred when a stream of air was bubbled for 3 hrs. through a soln. of the salt even in the presence of salts of cobalt, chromium, copper, and manganese which usually acted as carriers of oxygen. J. H. Reedy and J. S. Machin found that the reaction is positively catalyzed by manganese dioxide.

J. W. McBain, H. Vierling, E. Posnjak, J. A. N. Friend and E. G. K. Pritchett, W. A. Damon, I. K. Phelps, J. H. Reedy and J. S. Machin, P. K. Banerjee, and C. A. Peters and S. E. Moody also showed that the oxidation is a slow process, and J. W. McBain added that it increases with the conc. of the ferrous sulphate, and of oxygen, but it is not much affected by the acidity of the soln. although the presence of sulphuric acid has a retarding influence. P. K. Banerjee said that the reaction is slow, approximately unimolecular, and is hastened by the presence of potassium sulphate but retarded by other sulphates—particularly sulphuric acid and copper sulphate. E. Laska found that dil. soln. with about 0.24 per cent. of sulphuric acid resist oxidation in air between 15° and 96°. Thus, with 0.02*M*-FeSO<sub>4</sub>, the permanganate titre was initially 5.45; after 8 days, 5.43; 71 days, 5.37; 97 days, 5.37; and 123 days, 5.36; when 0.025*M*-H<sub>2</sub>SO<sub>4</sub> was also present, the initial titre was 5.5, and it remained 5.5 after 39 days. According to A. B. Lamb and L. W. Elder, the oxidation of soln. of ferrous sulphate by oxygen is greatly accelerated by increasing the rate of stirring the liquid; by increasing the conc. of the dissolved oxygen, the rate of oxidation increases in accord with the assumption that the reaction is unimolecular with respect to oxygen, as in the experiments of

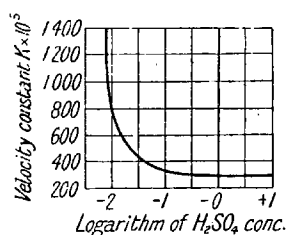


FIG. 646.—The Effect of the Acidity of the Solution on the Rate of Oxidation of Ferrous Sulphate.

J. W. McBain, and G. Just; and by increasing the conc. of the ferrous sulphate, the rate of oxidation increases in accord with the assumption that the reaction is bimolecular with respect to the ferrous salt as in the experiments of J. W. McBain, F. R. Ennos, and J. Boselli. The effect of varying the concentration of the sulphuric acid in the soln. is indicated by the curve, Fig. 646. J. Cornog and A. Herschberger found that there is but little oxidation when  $p_H < 5$ ; and with soln. buffered to  $p_H = 5$ , the degree of oxidation increased with increasing ion concentration, but at  $p_H = 10$ , it decreased with an increasing concentration of the iron. The percentage  $x$  of iron oxidized by aeration of the soln. of  $p_H = 5$  in  $t$  hrs. is:  $t = 0.032x - 0.01$ . The subject was studied by R. S. Martin, H. O. Halvorsen and R. L. Starkey, and L. Michaelis and C. V. Smythe; and the anodic oxidation, by A. Pletenew and W. N. Rosow.

The rate of oxidation is accelerated in the presence of salts of palladium, platinum, copper, and gold. E. Jordis and H. Vierling, and T. Warynsky also found that the oxidation of the soln. of ferrous salts is favoured by platinum salts. E. Laska, however, observed that the rate of oxidation is very little influenced by the presence of uranyl, vanadium, silver, zirconium, nickel, cerium, beryllium, stannous, and cobaltous salts, of ammonium chloride, or of arsenic trioxide. The activity of the catalysts increases more or less regularly with their concentration. The results are modified by variations of temp., such that there are certain limits within which the catalyst becomes more active with a rise of temp. Thus, with 0.02*M*-FeSO<sub>4</sub>, and 0.5*M*-CuCl<sub>2</sub>, the fall in the permanganate titre in 12 days, was:

96°	80°	60°	40°	15° (47 hrs.)
5.25→4.10	5.42→3.50	5.45→3.65	5.70→4.45	5.57→4.50

So that with this particular catalyst the activity increases with a rise of temp. from 15° to 80°, and then begins to decrease. E. M. Michelson, and J. W. McBain found that the rate of oxidation of 0.1*N*-FeSO<sub>4</sub> with *N*-H<sub>2</sub>SO<sub>4</sub> is increased 3- to 4-fold by a rise of temp. of 15°. E. Laska also found that the H<sup>+</sup>-ion concentration has

no influence, since he found that with different proportions of sulphuric acid, the permanganate titre of the 0.02*M*-FeSO<sub>4</sub> after 123 days changed from the initial value 5.43 :

H <sub>2</sub> SO <sub>4</sub>	0	2 <i>M</i> -	<i>M</i> -	0.5 <i>M</i> -	0.05 <i>M</i> -
Titre	5.37	5.42	5.39	5.41	5.40

and with boric acid in 0.02*M*-FeSO<sub>4</sub> with 0.025*M*-H<sub>2</sub>SO<sub>4</sub> :

H <sub>3</sub> BO <sub>3</sub>	0	0.25 <i>N</i> -	0.125 <i>N</i> -	0.0625 <i>N</i> -
Titre	5.37	5.31	5.30	5.29

This is not in accord with the results of other observers. In the presence of hydrochloric acid, with 0.02*M*-FeSO<sub>4</sub>, the titre fell in 123 days, from 5.43 :

HCl	0	2 <i>N</i> -	<i>N</i> -	0.5 <i>N</i> -	0.05 <i>N</i> -
Titre	5.37	4.70	5.30	5.34	5.42

so that hydrochloric acid favours the oxidation of the soln. This is attributed to the formation of some ferrous chloride:  $\text{FeSO}_4 + 2\text{HCl} \rightleftharpoons \text{H}_2\text{SO}_4 + \text{FeCl}_2$ , which is rather susceptible to atm. oxidation. Nitric acid in traces, has very little action, but with higher concentrations, it favours oxidation. Thus, with 0.02*M*-FeSO<sub>4</sub> with an initial titre of 5.43, in the presence of nitric acid, the titre fell to :

HNO <sub>3</sub>	0	0.05 <i>N</i> -	0.5 <i>N</i> -	<i>N</i> -	2 <i>N</i> -
Titre	5.37	5.15	0	0	0

A. B. Lamb and L. W. Elder observed that neutral salts—potassium, sodium, magnesium, zinc, manganous, nickel, and chromic sulphates, and sodium acetate or normal phosphate—have no appreciable effect on the oxidation of ferrous sulphate. The effects with copper sulphate are summarized in Figs. 647 and 648,

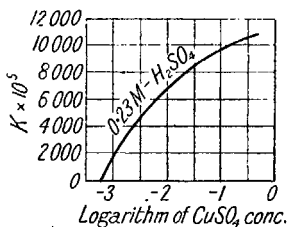


FIG. 647.—The Effect of Copper Sulphate.

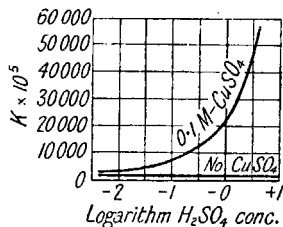


FIG. 648.—The Effect of Acid and Copper Sulphate.

and the curves indicate that the acceleration produced by copper sulphate increases with its concentration, and with the acidity of the soln. This confirms the observations of J. Boselli, and J. Cornog and A. Herschberger, contrasted with those of P. K. Banerjee. The rate of oxidation with 0.023*M*-sodium pyrosulphate is quickened about 1000 times, and this the more, as shown by J. H. C. Smith and H. A. Spoehr, the faster is the rate of stirring. The presence of steam-activated, coco-nut charcoal, or of platinum black hastens the reaction; the accelerating effect with silica gel is small. The reaction is retarded by phenyl urea, amyl alcohol, and acetanilide.

E. Posnjak's observations on the oxidation of ferrous sulphate soln. in the presence of copper sulphate, as catalyst, do not agree with those of E. Laska. The copper sulphate accelerates the rate of oxidation to a marked degree. The results with 0.1*N*- and 0.5*N*-FeSO<sub>4</sub>, with and without 0.0036*M*-CuSO<sub>4</sub>, are shown in Fig. 649. The oxidation follows the rule for bimolecular reactions,  $k = x/ta(a-x)$ , where  $k$ , without catalyst, is 0.00016, and 0.0035 for 0.1*N*-FeSO<sub>4</sub> with 0.0036*M*-CuSO<sub>4</sub>, and 0.00052 for 0.5*N*-FeSO<sub>4</sub> with 0.0036*M*-CuSO<sub>4</sub>. The acceleration due to the presence of copper sulphate is explained by E. Posnjak on the assumption that a state of equilibrium is set up in the soln.  $2\text{FeSO}_4 + 2\text{CuSO}_4$

$\rightleftharpoons \text{Fe}_2(\text{SO}_4)_3 + \text{Cu}_2\text{SO}_4$ , or  $\text{Fe}^{++} + \text{Cu}^{++} \rightleftharpoons \text{Fe}^{+++} + \text{Cu}^+$ . This is supported by the observations of H. C. Biddle, L. Maquenne and E. Demousay, F. Herrmann, E. Müller and F. Kapeller, J. A. Verhoeff, P. K. Banerjee, H. R. Ellis and W. H. Collier, and C. van Brunt. E. Posnjak said that the cuprous salt is readily oxidized, and that the acceleration produced by cupric sulphate is due to the oscillation of some of the copper between two stages of oxidation, which, combined with the equilibrium existing between ferrous and cupric ions, is probably responsible for the rapid formation of the ferric salt in soln. The effectiveness of the cupric sulphate decreases with increasing conc. of ferric ions in accord with the theory. A. B. Lamb and L. W. Elder found that those substances which, according

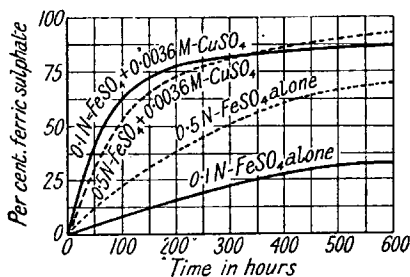


FIG. 649.—The Rate of Oxidation of Solutions of Ferrous Sulphate.

ing to G. Lemoine, O. Warburg, and V. L. Bohnson and A. C. Robertson, hasten the decomposition of hydrogen dioxide—e.g., charcoal, platinum, and cupric salts—in the presence of ferrous salts, also accelerate the oxidation of ferrous sulphate soln. It has been suggested that the oxidation process involves the formation of hydrogen dioxide:  $2\text{FeO} + \text{O}_2 + \text{H}_2\text{O} = \text{Fe}_2\text{O}_3 + \text{H}_2\text{O}_2$ , by a slow primary reaction followed by the rapid reaction:  $2\text{FeO} + \text{H}_2\text{O}_2 = \text{Fe}_2\text{O}_3 + \text{H}_2\text{O}$ , but A. K. Goard and E. K. Rideal observed that copper salts do not catalyze the oxidation of ferrous salts by hydrogen dioxide in acidic soln. It is very unlikely that hydrogen dioxide is formed by the action of oxygen on water since the equilibrium partial press. of hydrogen dioxide in a 1 : 1 gaseous mixture of oxygen and air is of the order of  $10^{-22}$  atm. Hence it is doubtful if hydrogen dioxide is the effective agent in these oxidations. It is more likely that the catalysis is due to the formation of specific peroxides, minute quantities of such a substance have been extracted from aerated charcoal by means of sulphuric acid.

R. Thomas and E. T. Williams, and N. McCulloch also observed that the presence of nitric oxide favours the oxidation of ferrous sulphate soln. According to W. S. Hendrixson, when ferrous iron is added to a dil. soln. of an oxidizing agent in sulphuric acid, there is a rise in the potential of electrodes by accelerating the rate at which they take up their full charges. In all but extremely dil. soln., the electrodes reach saturation after several hours, and normal falls of potential are then produced by the addition of ferrous sulphate. For the basic salt **ferrous oxysulphate**,  $\text{FeO} \cdot \text{FeSO}_4$ , *vide supra*, the electrolysis of soln. of ferrous sulphate. W. Feitknecht found that the space-lattice of  $\text{FeSO}_4 \cdot 3\text{Fe}(\text{OH})_2$  corresponds with alternate layers of hydroxide and of the normal salt.

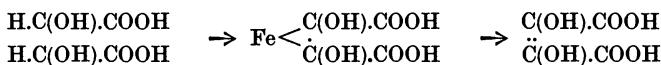
In alkaline soln., E. Müller and F. Kapeller found that the oxidation is fairly rapid. The oxidation of certain soln. of ferrous salts may be accelerated by certain micro-organisms called iron bacteria, examples of whose action in the production of natural deposits of bog-iron ore were discussed in connection with limonite. E. M. Mumford, indeed, showed that bacteria were able completely to oxidize a dil. soln. of ammonium ferrous sulphate into hydrated ferric oxide in 36 hrs. at  $37^\circ$ .

The general results show that to prevent the oxidation of soln. of ferrous sulphate the soln. can be made up with well-boiled water, and kept in an atmosphere of an inert gas—hydrogen (N. A. Tananaeff), nitrogen (J. A. Hedvall and J. Heuberger), or carbon dioxide (G. Bailhache). Contact of the soln. with iron (O. Mustad) is not satisfactory. A layer of an inert liquid like benzene (F. W. Horst) over the soln. is moderately successful for a few days. F. K. Cameron observed that at higher temp., an atmosphere of water vapour will prevent access of oxygen enabling the soln. to be kept for some weeks, and at a lower temp. a few per cent. of alcohol has proved effective.

The solubility of ferrous sulphate in **water**, and the conditions of equilibrium of the various hydrates, have been discussed previously; the hydrolysis of the salt in aq. soln. has also been described. A. K. Bhattacharya and N. R. Dhar found that with a sulphuric acid soln. in light of wave-length 8500 Å.:

Velocity coeff.	{ in dark . . .	30°	0.00377	0.000675	0.00112
	{ in light . . .		0.00903	0.00153	0.00246
Quantum efficiency for 8500 Å. .			5.4	8.9	13.4

The temp. coeff. of the reactions are less in light than in darkness. P. Rohland observed that "burnt" and powdered ferrous sulphate "sets" when mixed with water almost as if the salt were plaster of Paris. A. Krause studied the hydrolysis of ferrous sulphate and found that the H<sup>+</sup>-ion conc. is  $p_H=3.5$ , whereas that for ferric sulphate is  $p_H=1.3$  in agreement with the fact that ferrous hydroxide is a stronger base than ferric hydroxide. The iso-electric point for ferrous hydroxide soln. is  $p_H=11.5$ , and for ferric hydroxide  $p_H=7.7$ . According to C. Weltzien, **hydrogen dioxide** precipitates  $2Fe_2O_3 \cdot SO_3 \cdot 8H_2O$  from aq. soln. of ferrous sulphate:  $6FeSO_4 + 3H_2O_2 = 2Fe_2O_3 \cdot SO_3 + 3H_2O + Fe_2O_3 \cdot 5SO_3$ . C. F. Schönbein showed that in many reactions, iron salts can act as carriers of oxygen, and H. J. H. Fenton explained the oxidation of tartaric acid to dihydroxymaleic acid in the presence of, say, ferrous sulphate, by assuming that bivalent iron replaces the two non-hydroxylic hydrogen atoms. The ferrous iron of the intermediate compound is then oxidized, and the tervalent iron breaks away leaving dihydroxymaleic acid:



The reaction was studied by A. T. Küchlin, F. Haber and J. Weiss, D. R. Hale, and W. Manchot. W. Manchot and co-workers, and J. Brode suggested that in the case of hydrogen dioxide, the iron is converted into an unstable, complex higher oxide,  $Fe_2O_5$ , or  $Fe_2O_3 \cdot 2H_2O_2$ —the primary oxide of W. Manchot—which is then reduced by the oxidizable substance. C. S. Mummery supposed that the ferrous sulphate unites with the hydrogen dioxide to form what he called a perhydrol,  $HSO_4 \cdot Fe \cdot O \cdot OH$ . It is supposed that the monohydrated ferrous sulphate has the constitution:  $HSO_4 \cdot Fe \cdot OH$ , which then reacts with hydrogen dioxide:  $HSO_4 \cdot Fe \cdot OH + HO \cdot OH \rightleftharpoons HSO_4 \cdot Fe \cdot O \cdot OH + H_2O$ . This imaginary product is supposed to be analogous with monopersulphuric acid,  $HO \cdot SO_2 \cdot O \cdot OH$ , and, in consequence, the product is assumed to be a powerful oxidizer. The hypothetical perhydrol is assumed to be alternately formed and decomposed in a never-ending cycle so long as the oxidizable substance and hydrogen dioxide are present. D. R. Hale, R. Kuhn and A. Wassermann, S. Goldschmidt and co-workers, and E. Spitalsky and N. Petin studied the reaction between hydrogen dioxide, ferrous sulphate, and potassium iodide—*vide* ferric sulphate and hydrogen dioxide. The activity of ferrous sulphate was found by A. M. Malkoff and N. Zvetkova to be retarded by phosphate. N. N. Biswas and N. R. Dhar studied the chemiluminescence of organic substances in the presence of ferrous sulphate and hydrogen dioxide. H. Kwasnik found that an aq. soln. of ferrous sulphate reacts with **barium dioxide** giving off oxygen and forming hydrated ferric oxide; but H. Frischer said that **sodium dioxide** and barium dioxide under these conditions give off no oxygen and precipitate basic ferric sulphate,  $Fe_2(OH)_4SO_4$ .

According to K. H. Butler and D. McIntosh, heptahydrated ferrous sulphate is insoluble in liquid **chlorine**. Aq. soln. of the salt are oxidized by the halogens; thus, when gaseous chlorine acts on the soln., ferric sulphate and chloride are produced and the thermal value of the reaction is 24.436 Cals. per mol. of  $FeSO_4$ . The reaction with chlorine and **bromine** was discussed by M. C. Schuyten; A. W. Francis studied the speed of the reaction with bromine. M. C. Schuyten investigated the action of **iodine**; A. Berthoud and S. von Allmen, R. C. Banerji and N. R. Dhar, B. K. Mukerji and N. R. Dhar, A. K. Bhattacharya and N. R. Dhar, and N. R. Dhar,



the photochemical oxidation of a soln. of ferrous sulphate by iodine; and D. R. Hale studied the induced reaction between ferrous sulphate, potassium iodide, and hydrogen dioxide. The use of iron salts as halogen carriers in organic chemistry was discussed by B. Aronheim, L. Meyer, L. Meyer and A. Scheufelen, A. G. Page, A. Scheufelen, and C. Willgerodt. G. B. Heisig, and A. C. Christomanos found that a soln. of ferrous sulphate is oxidized to a ferrous salt by **iodine trichloride**. R. Kane said that anhydrous ferrous sulphate is indifferent towards gaseous **hydrogen chloride**, but at an elevated temp., when the thermal decomposition of the sulphate is proceeding, C. Hensgen observed that ferric chloride is formed. F. Ephraim observed that no complex is formed with hydrogen chloride. G. Gore found that in liquefied hydrogen chloride the heptahydrate becomes yellowish-white and opaque, without dissolving. R. Kane said that the salt is soluble in hot **hydrochloric acid**. A. L. Young and G. F. Dixon found that when a gram of the heptahydrate mixed with 3.5 c.c. of hydrochloric acid, of sp. gr. 1.153, is evaporated on a water-bath, 2.3 per cent. of the iron is converted into chloride. C. Hensgen observed that when a conc. soln. of ferrous sulphate is saturated with hydrogen chloride, pale green needles of  $\text{FeCl}_3 \cdot \text{H}_2\text{O}$ , and tabular plates of  $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$  separate from the soln. A. J. Balard found that ferrous sulphate is oxidized to ferric sulphate by **hypochlorous acid** and **hypochlorites**:  $2\text{Fe}^{++} + \text{H}^+ + \text{HOCl} = 2\text{Fe}^{+++} + \text{Cl}^- + \text{H}_2\text{O}$ . The reaction was discussed by J. Dalton, C. R. A. Wright, T. Wittstein, E. Biltz, and N. Graeger. Ferrous sulphate reacts instantly with **chlorine dioxide**; K. von Garzarolli-Thurnlackh and K. von Hayn represent the reaction:  $\text{ClO}_2 + 5\text{Fe}^{++} + 4\text{H}^+ = \text{Cl}^- + 5\text{Fe}^{+++} + 2\text{H}_2\text{O}$ ; and E. Lenssen added that if an aq. soln. of chlorine dioxide be added to a dil. acidic soln. of a ferrous salt, an amethyst colour first appears, and this changes to yellow after a few seconds. W. Oechsli represented the reaction with **barium chlorite**:  $\text{Ba}(\text{ClO}_2)_2 + 8\text{FeSO}_4 + 5\text{H}_2\text{SO}_4 = 4\text{Fe}_2(\text{SO}_4)_3 + 2\text{HCl} + \text{BaSO}_4 + 4\text{H}_2\text{O}$ ; the ferrous sulphate was found by A. Schleicher and W. Wesly not to be oxidized in neutral soln. C. R. A. Wright showed that ferrous sulphate in acidic soln. is oxidized by **chloric acid**, and that the speed of the reaction is dependent on the temp., and on the conc. of the acid in the soln.; and A. Carnot, and M. Herschkowitsch said that the reaction is quantitative; but with aluminium chlorate, D. K. Dobrosserdoff found that the reduction is only partial. J. J. Hood found that the speed of the reaction is retarded by sodium, potassium, ammonium, lithium, magnesium, zinc, and cadmium sulphates, by potassium and ammonium chlorides, and by potash-alum, and ammonium-alum; sodium chloride has very little effect; whilst magnesium, zinc, and cadmium chlorides accelerate the reaction; T. F. Rutter showed that the reaction is also accelerated by vanadium salts. W. F. Green said that the reaction is not affected by the presence of ferric salts. R. R. Enfield studied the accelerating influence of acids; J. J. Hood represented the reaction in the presence of an excess of acid by  $6\text{Fe}^{++} + \text{ClO}_3^- + 6\text{H}^+ = 6\text{Fe}^{+++} + \text{Cl}^- + 3\text{H}_2\text{O}$ , and said that the reaction is of the second order with the velocity proportional to the product of the concentrations of the two salts, the acid exerting an accelerative influence, the velocity increasing rather more rapidly than the acid concentration, but A. A. Noyes and R. S. Wason represented it as a reaction of the third order; the reaction appears of the second order only when an excess of acid is present. The reaction was studied by F. H. MacDougall, C. F. Schönbein, D. Vitali, F. Becker, C. O. Harvey, W. Bray, and W. F. Green. F. Bellamy observed that in consequence of the acid nature of anhydrous ferrous sulphate, its presence accelerates the thermal decomposition of **potassium chlorate**, with the formation of chlorine; and M. Herschkowitsch added that a well-dried mixture of the two salts does not react at  $100^\circ$ ; but if the mixture be moistened with a few drops of water, or if commercial sulphate or the heptahydrate be used, chlorine, hydrogen chloride, and chlorine dioxide are evolved, and ferric sulphate and chloride remain. L. C. A. Barreswil observed that a soln. of potassium chlorate and ferrous sulphate in the cold gives a red precipitate of a hydrated basic ferric salt, whilst a hot soln. yields a yellow,

anhydrous precipitate sparingly soluble in acids. A mixture of hydrochloric acid and potassium chlorate oxidizes ferrous sulphate to a ferric salt. The reduction of chlorates in alkaline soln. by ferrous sulphate was found by C. Stelling to be quantitative. Observations were made by F. Becker, I. Bhaduri, N. R. Dhar, M. Couleru, C. O. Harvey, I. K. Phelps, C. Russo and G. Sensi, and E. C. Wagner. Soluble iodides reduce chlorates to chlorides:  $\text{KClO}_3 + 6\text{KI} + 3\text{H}_2\text{SO}_4 = \text{KCl} + 3\text{K}_2\text{SO}_4 + 3\text{I}_2 + 3\text{H}_2\text{O}$ ; the reaction is greatly accelerated by the presence of ferrous or ferric salts; and, according to W. D. Bonner and H. Romeyn, the reaction  $\text{Fe}^{++} + \frac{1}{2}\text{I}_2\text{Aq.} = \text{Fe}^{+++} + \text{I}^-$  goes to an end in the presence of a phosphate and a moderate concentration of acid. In the former case, W. F. Green, and L. Pisarschewsky and N. Averkéeff assumed that the iodine forms ferrous iodide which is then oxidized to the ferric salt, and that the catalytic effect is due to the cyclic formation and decomposition of ferric iodide:  $\text{KClO}_3 + 6\text{FeI}_2 + 6\text{KI} + 3\text{H}_2\text{SO}_4 = \text{KCl} + 3\text{K}_2\text{SO}_4 + 6\text{FeI}_3 + 3\text{H}_2\text{O}$ , and  $2\text{FeI}_3 = 2\text{FeI}_2 + \text{I}_2$ . C. Löwig observed that **potassium bromate** reacts with a soln. of ferrous sulphate forming a brownish-red precipitate which is probably ferrous bromate. According to S. E. Moody, hydrolysis occurs when a soln. of ferrous sulphate is boiled with **potassium iodate** and iodide:  $3\text{FeSO}_4 + 5\text{KI} + \text{KIO}_3 + 3\text{H}_2\text{O} = 3\text{Fe}(\text{OH})_2 + 3\text{K}_2\text{SO}_4 + 3\text{I}_2$ ; and the excess of iodate then oxidizes the hydrated ferrous to ferric oxide:  $6\text{Fe}(\text{OH})_2 + \text{KIO}_3 + 3\text{H}_2\text{O} = \text{KI} + 6\text{Fe}(\text{OH})_3$ . The subject was studied by G. B. Heisig.

The reaction between **sulphur** and ferrous sulphate:  $\text{FeSO}_4 + 2\text{S} = \text{FeS} + 2\text{SO}_2$ , studied by F. Stolba, H. Schiff, E. Glatzel, and H. Rose, has been discussed in connection with the preparation of ferrous sulphide and iron disulphide; K. Brückner noted that some iron disulphide is formed. G. Vortmann and C. Padberg observed no chemical change occurs when a soln. of ferrous sulphate is boiled with sulphur. The action of **hydrogen sulphide** has been discussed in connection with the preparation of ferrous sulphide and of iron disulphide. The action of **ammonium and alkali sulphides** has been indicated in connection with the reactions of analytical interest. The aq. soln. was found by E. Schürmann to be completely decomposed by **manganese sulphide**, and partially decomposed by **thallous, cobalt, and nickel sulphides**, and only a little decomposed by zinc sulphide. The reaction with eq. quantities of cobalt, or nickel, sulphide, with ferrous sulphide results in the formation of a complex sulphide; and F. Feigl said that when the ratio of cobalt or nickel sulphide to the iron in the ferrous sulphide is as 2 : 1, approximately 30 per cent. of the iron in the salt is transformed. J. d'Ans, and G. Keppeler and J. d'Ans observed that the anhydrous sulphate above  $600^\circ$  decomposes in a current of **sulphur dioxide**, and that the result is the same as if the sulphate had been heated in an indifferent gas; no ferrous oxide is formed; the products of the reaction are ferric oxide, and sulphur dioxide and trioxide. L. Meyer found that ferrous sulphate comes after manganous and copper salts in the order of activity as a catalyst in the oxidation of sulphur dioxide. K. F. Ochs studied the subject. C. F. Schönbein observed that if the crystals of the heptahydrate are quite free from ferric sulphate they remain colourless when treated with sulphurous acid, but if a trace of ferric sulphate be present, the colour changes to yellowish-brown.

According to A. Bussy and L. R. Lecanu, anhydrous or heptahydrated ferrous sulphate is soluble in conc. **sulphuric acid**, of sp. gr. 1.843, forming a rose- or purple-coloured liquid; and E. Divers and T. Shimidzu, G. Fownes, W. B. Giles, and T. Scheerer found that when the heptahydrate is boiled with conc. sulphuric acid, sulphur dioxide is evolved:  $2\text{FeSO}_4 + 2\text{SO}_3 = \text{Fe}_2(\text{SO}_4)_3 + \text{SO}_2$ . J. Kendall and A. W. Davidson observed that mixtures of 0.22, 0.31, 0.40, 0.51, and 0.63 per cent. of anhydrous ferrous sulphate and sulphuric acid had the respective f.p.  $30.2^\circ$ ,  $42.3^\circ$ ,  $48.6^\circ$ ,  $57.7^\circ$  and  $63.8^\circ$ . The upward slope of the curve indicates that an acid salt is present. The f.p. of higher concentrations were not measured because the mixtures became cloudy owing to the oxidation of the ferrous sulphate, by the sulphuric acid, to the less soluble ferric sulphate. The effect of sulphuric acid in retarding the aerial oxidation of a soln. of ferrous sulphate has been previously



V. Komar reported crystals of normal **ferrous hydrosulphate**,  $\text{FeO} \cdot 2\text{SO}_3 \cdot \text{H}_2\text{O}$ , or  $\text{FeSO}_4 \cdot \text{H}_2\text{SO}_4$ , or  $\text{Fe}(\text{HSO}_4)_2$ , to be formed by the evaporation of a soln. of ferrous sulphate with sulphuric acid of sp. gr. 1.3 to 1.4. F. B. Kenrick observed it to be the solid phase in the ternary system  $\text{FeSO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$  at  $25^\circ$  with soln. containing  $\text{SO}_3$  :  $1.342\text{H}_2\text{O}$  to  $1.595\text{H}_2\text{O}$ . The prismatic crystals are well-formed, and, under the microscope, resemble those of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ . It is thought that this salt may be identical with the *ferrous pyrosulphate*,  $\text{FeS}_5\text{O}_2$ , reported by T. Bolas to be formed by cooling a mixture of 9 vols. of conc. sulphuric acid with 1 vol. of a sat. soln. of ferrous sulphate. F. B. Kenrick obtained small, colourless, hexagonal crystals of **ferrous hydrosulphatosulphate**,  $2\text{FeO} \cdot 3\text{SO}_3 \cdot 2\text{H}_2\text{O}$ , or  $2\text{FeSO}_4 \cdot \text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ , or  $\text{FeSO}_4 \cdot \text{Fe}(\text{HSO}_4)_2 \cdot \text{H}_2\text{O}$ , from soln. containing between  $\text{SO}_3$  :  $1.637\text{H}_2\text{O}$  to  $\text{SO}_3$  :  $2.186\text{H}_2\text{O}$ . It is thought that the crystals may be the same as those reported by F. Jeremin to contain  $\text{FeSO}_4 \cdot 5\text{H}_2\text{SO}_4 \cdot 5\text{H}_2\text{O}$ , or  $\text{FeO} \cdot 6\text{SO}_3 \cdot 10\text{H}_2\text{O}$ , i.e. **ferrous pentahydrosulphatosulphate**; F. Jeremin prepared this salt, in unstable, greenish crystals, by rapidly mixing a sat. soln. of ferrous sulphate with at least 4 vols. of sulphuric acid of sp. gr. 1.83. P. A. von Bonsdorff obtained colourless plates, sparingly soluble in water, and of the composition **ferrous trihydrosulphatosulphate**,  $\text{FeO} \cdot 4\text{SO}_3 \cdot 3\text{H}_2\text{O}$ , or  $\text{FeSO}_4 \cdot 3\text{H}_2\text{SO}_4$ , by mixing conc. soln. of ferrous sulphate and sulphuric acid until the sp. gr. is 1.33; evaporating the liquid over conc. sulphuric acid until its sp. gr. is 1.50; and crystallizing. F. B. Kenrick said that the salt is stable in soln. with between  $\text{SO}_3$  :  $1.22\text{H}_2\text{O}$  to  $\text{SO}_3$  :  $1.342\text{H}_2\text{O}$ .

M. Berthelot observed that when **persulphuric acid** is dropped into an acidic soln. of ferrous sulphate, an unstable brown product is formed which with further additions of acid is decomposed to form a colourless soln. R. N. J. Saal, and T. S. Price studied the catalytic action of ferrous salts on the reaction between **persulphates** and iodides:  $\text{K}_2\text{S}_2\text{O}_8 + 2\text{KI} = 2\text{K}_2\text{SO}_4 + \text{I}_2$ . According to G. Lunge, sulphuric acid containing **selenium dioxide** gives a brownish-yellow, or yellowish-red ring when dropped into a soln. of ferrous sulphate, the colour does not vanish when the liquid is warmed as is the case with the brown ring formed by nitric oxide. E. Keller observed that a soln. of selenium dioxide in hydrochloric acid, exceeding 30 per cent. HCl, deposits all the selenium in 24 hrs., but **tellurium dioxide** under similar conditions does not react with the hydrochloric acid. F. D. Crane observed that the precipitation of tellurium with ferrous sulphate soln. occurs only when the soln. of tellurium tetrachloride is free from the dichloride.

E. C. Franklin and C. A. Kraus observed that ferrous sulphate is insoluble in liquid **ammonia**. According to F. Ephraim, when ammonia is passed over anhydrous ferrous sulphate, heat is evolved and the salt swells up forming a voluminous, white powder whose composition is not far from  $\text{FeSO}_4 \cdot 6\text{NH}_3$ ; if the temp. be raised high enough, W. R. Hodgkinson and C. C. Trench observed that the anhydrous or hydrated sulphate is reduced to iron containing 1 to 2 per cent. of sulphur. The action of ammonia on hydrated ferrous sulphate or on aq. soln. furnishes a series of amines. A. Kaufmann observed that when reduced iron is dissolved in a hot, ammoniacal, saturated soln. of ammonium sulphate, the yellow soln. probably contains ferrous aminosulphate, though none was isolated. F. Ephraim prepared **ferrous hexamminosulphate**,  $\text{FeSO}_4 \cdot 6\text{NH}_3$ , or  $[\text{Fe}(\text{NH}_3)_3]\text{SO}_4$ , by passing ammonia over anhydrous ferrous sulphate. The voluminous, white powder is readily oxidized. Its dissociation press.,  $p$  mm., is:

	73°	82°	88.5°	94.5°	96°	98.5°	102.5°	107°	108°	109.5°
$p$ . . .	150	256	350	464	500	551	642	740	760	788

The compound is stable up to  $91^\circ$ , beyond which it begins to form the tetrammine, Fig. 651. The heat of dissociation to the tetrammine is 13.65 Cals. per mol. of ammonia. F. Ephraim discussed the relation between the dissociation temp. and the at. vol. F. Müller gave  $-18^\circ$  to  $75^\circ$  for the temp. of dissociation of the heptammine. E. Weitz and H. Müller were unable to prepare the hexammine by

wet processes; the nearest they could produce was **ferrous pentamminosulphate**,  $\text{FeSO}_4 \cdot 5\text{NH}_3 \cdot \text{H}_2\text{O}$ , or *ferrous aquopentamminosulphate*,  $[\text{Fe}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{SO}_4$ , which they obtained, in green, rhombohedral crystals, by driving out the air from a soln. of 5 grms. of Mohr's salt in 200 c.c. of water, passing ammonia into the well-

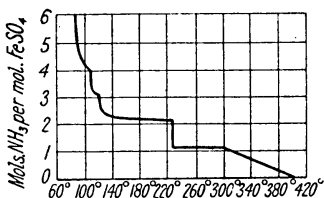


FIG. 651. — The Dissociation Curve of the Ferrous Amminosulphates.

cooled liquid so that the hydroxide first precipitated is redissolved, filtering in an atm. of ammonia, and allowing the soln. to crystallize. F. Müller gave 75° to 95° for the dissociation temp. of the pentammine. J. A. Verhoeff employed an analogous process, but precipitated the salt by the addition of alcohol sat. with ammonia to the well-cooled liquid. F. Ephraim observed that when the hexammine is heated to nearly 110°, it forms **ferrous tetramminosulphate**,  $\text{FeSO}_4 \cdot 4\text{NH}_3$ , with a dissociation press. of 500 mm. at 117°, and 760 mm. at 125°—Fig. 651. He studied the relation between the dissociation temp. and the at. vol.; and found for the heat of dissociation to the diammine, 14.32 Cals. per mol. of ammonia. W. Peters obtained a *monohydrate*,  $\text{FeSO}_4 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$ , or  $[\text{Fe}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ , by the action of ammonia on monohydrated ferrous sulphate, at room temp. When kept in vacuo, this salt passes into the diammine. G. Spacu prepared the same salt by passing a brisk current of dry ammonia over the pyridine sulphate,  $[\text{Fe}(\text{C}_5\text{H}_5\text{N})_3(\text{H}_2\text{O})]\text{SO}_4 \cdot \text{H}_2\text{O}$ . It is almost insoluble in water; and is hydrolyzed in aq. soln.; it is insoluble in most solvents, but it dissolves in dil. sulphuric acid. F. Müller gave 95° to 110° for the dissociation temp. F. Ephraim found that **ferrous triamminosulphate**,  $\text{FeSO}_4 \cdot 3\text{NH}_3$ , is formed when the higher ammine is heated between 120° and 123°—Fig. 651—and W. Peters obtained the *monohydrate*,  $\text{FeSO}_4 \cdot 3\text{NH}_3 \cdot \text{H}_2\text{O}$ , by the action of ammonia on the hydrated diammine. F. Ephraim found that the triammine passes into **ferrous diamminosulphate**,  $\text{FeSO}_4 \cdot 2\text{NH}_3$ , when heated to 221° to 222°; and W. Peters prepared the *monohydrate*,  $\text{FeSO}_4 \cdot 2\text{NH}_3 \cdot \text{H}_2\text{O}$ , by keeping the hydrated tetrammine in vacuo. F. Ephraim prepared **ferrous monamminosulphate**,  $\text{FeSO}_4 \cdot \text{NH}_3$ , by heating a higher ammine between 300° and 400°—Fig. 651. F. Müller gave 180° to 190° for the dissociation temp. of the diammine, and 192° to 225° for that of the monammine. H. Weitz observed that no nitrosyl ammine is formed when nitric oxide is passed into an ammoniacal soln. of ferrous and ammonium sulphates. O. R. Foz and L. le Boucher studied the amminosulphates.

H. A. von Vogel found that on adding a soln. of **ammonium chloride** to one of ferrous sulphate, a complex salt is formed. A. Kurtenacker and F. Werner studied the catalytic decomposition of **hydroxylamine** by ferrous sulphate. According to T. W. B. Welsh and H. J. Broderson, ferrous sulphate is only slightly soluble in liquid **hydrazine**, gas is evolved, and a yellow precipitate is formed. The soln. is a poor conductor of electricity; and a black deposit appears on the cathode, and it is soluble in hydrochloric acid. H. Schjerring said that ferrous sulphate and **phenylhydrazine** form the complex salt. T. Curtius and J. Rissom, and L. M. Dennis and A. W. Browne noted that **sodium azide**, when shaken in air with a soln. of ferrous sulphate, develops a blood-red coloration. C. T. Dowell and W. C. Bray found that when a soln. of ferrous sulphate is treated with a soln. of **nitrogen trichloride**,  $\text{NCl}_3$ , in carbon tetrachloride, an ammonium salt is formed, and nitrogen is evolved. According to W. Manchot and co-workers, aq. soln. with 0, 10.938, and 21.845 grms. of  $\text{FeSO}_4$  per 100 c.c. dissolve respectively 53.3, 34.0, and 21.6 c.c. of **nitrous oxide** per 100 c.c. of soln. According to V. Thomas, unlike ferrous chloride and bromide, anhydrous ferrous sulphate absorbs no **nitric oxide**; but J. Priestley observed that a soln. of ferrous sulphate is coloured dark brown by nitric oxide, and when the sat. aq. soln. is treated with the gas, W. Manchot and co-workers—F. Huttner, H. Haunschild, and E. Linckh—observed the

formation of **ferrous nitrosylsulphate**,  $\text{FeSO}_4\cdot\text{NO}$ , and of **ferrous heminitrosylsulphate**,  $2\text{FeSO}_4\cdot\text{NO}\cdot 13\text{H}_2\text{O}$ . The reaction was studied by E. Péligré, H. Davy, F. H. A. von Humboldt and L. N. Vauquelin, L. Cambi and A. Clerici, W. Kalle and W. Prickarts, G. von Hüfner, L. Carius, V. A. Jacquelin, A. Bussy and L. R. Lecanu, E. Desbassyns de Richemont, J. Gay, F. Raschig, F. L. Usher, E. Lenssen, etc.—*vide* 8, 49, 35. J. Bystron and K. von Vietinghoff observed that when **nitrogen peroxide** is passed into a soln. of ferrous sulphate, a basic ferric salt is precipitated. A. Thum found that a soln. of **alkali hyponitrite** reacts with a freshly-prepared soln. of ferrous sulphate forming a light green precipitate which soon becomes darker, while the soln. becomes strongly acidic. Ferrous salts reduce **nitrites** to nitric oxide, owing, said P. Piccini and F. M. Zuco, to the formation of an unstable ferrous nitrite:  $6\text{Fe}(\text{NO}_2)_2 = 10\text{NO} + \text{Fe}_2\text{O}_3 + 2\text{Fe}_2\text{O}_3\cdot\text{N}_2\text{O}_5$ . A. Thiele said that the reaction with a conc. soln. of sodium nitrite and a hydrochloric acid soln. of ferrous sulphate can be used for making nitric oxide of a high degree of purity. When **nitric acid** is added to a soln. of ferrous sulphate, acidified with sulphuric acid, nitric oxide is formed:  $6\text{FeSO}_4 + 3\text{H}_2\text{SO}_4 + 2\text{HNO}_3 = 3\text{Fe}_2(\text{SO}_4)_3 + 4\text{H}_2\text{O} + 2\text{NO}$ . The latter produces a brown coloration which is applied in the so-called *ring-test* for nitric acid and the nitrates, where a cold soln. of ferrous sulphate is poured down the sides of a test-tube containing a layer of conc. sulphuric acid and the suspected nitrate. If a nitrate is present, the colour of the ring at the junction of the two liquids will be ruddy if the nitrosyl compound is formed in the conc. acid layer, and brown, if formed in the aq. soln. The coloration was also applied by L. Maugé, F. C. Bowman and W. W. Scott, and I. Bellucci to the volumetric determination of nitric acid. The brown colour is formed only in the presence of an excess of ferrous sulphate, and when nitric acid is added, the remaining ferrous sulphate is oxidized completely, and the colour then disappears. The production of the brown coloration was utilized, by L. Blum, to detect the presence of ferrous salts in the presence of the salts of some other metals. As shown by N. A. E. Millon, and V. H. Veley, ferrous sulphate retards the action of nitric acid on metals, and this is attributed by P. C. Ray to the destruction of nitrous acid during the catalytic or cyclic oxidation and reduction of the iron salt.

C. H. Knoop found that when heptahydrated ferrous sulphate is mixed with powdered phosphorite, and heated to  $250^\circ$ , the phosphate becomes soluble in a soln. of citric acid. T. Salzer observed that **hypophosphoric acid** or **sodium hypophosphate** produces a white precipitate with a soln. of ferrous sulphate. R. Meissner found that when **arsine** is passed into a soln. of ferrous sulphate, only 1 to 3 per cent. is absorbed. D. R. Hale studied the induced reaction with ferrous sulphate, potassium permanganate, and **sodium arsenite**. E. Schürmann observed that **arsenic sulphide** reacts partially with ferrous sulphate in aq. soln.

P. Berthier said that when ferrous sulphate is heated with **carbon** in a carbon crucible, ferrous sulphide is formed; and J. L. Gay Lussac observed that when the mixture is heated in a retort, sulphur and carbon dioxides are evolved, and ferric oxide free from sulphide is formed; at a higher temp., the oxide is reduced to metal: A. G. Doroschewsky and A. J. Bardt observed that ferrous sulphate intensifies the catalytic action of carbon in the oxidation of alcohols. N. Schiloff and L. Lepin studied the adsorption of ferrous sulphate from a 0.05*N*-soln. by carbon. W. A. Jakowenko found that the heptahydrate reacts with **calcium carbide** giving off the equivalent of 5.9 mol. of water in the form of acetylene. According to W. Manchot and co-workers, soln. with 0, 10.938, and 21.845 grms. of  $\text{FeSO}_4$  per 100 c.c., dissolve 95.7, 61.6, and 41.1 c.c. of **acetylene** at  $25^\circ$ . C. Doelter observed that when the heptahydrate is heated in coal-gas, it is reduced to ferrous sulphide. The salts of iron are reduced to metal when heated in **carbon monoxide**, and G. P. Schweder found that when ferrous sulphate is heated in an atm. of carbon monoxide, a mixture of ferrous sulphide with iron or ferric oxide is formed. J. H. Weibel studied the action of the gas under press. on the aq. soln. E. H. Büchner, and G. Gore found that the heptahydrate is not dis-

solved by liquid **carbon dioxide**, but the salt is transformed into a white powder. A. Conduché observed that when ferrous sulphate is heated in **chloroform** vapour, it produces a mixture of ferrous and ferric chlorides from which the latter sublimes. E. Alberts similarly investigated the action of the vapour of **carbon tetrachloride**. J. Barlot and E. Chauvenet found that the anhydrous sulphate reacts with **carbonyl chloride** at  $300^{\circ}$  to  $500^{\circ}$  forming ferrous chloride, sulphuryl chloride, and carbon dioxide. According to A. W. Davidson, when ferrous sulphate is mixed with 100 per cent. sulphuric acid, and **potassium ferricyanide**, the brown colour disappears without showing any other evidence of a reaction; when the mixture is diluted with water, a blue precipitate is formed. Ferrous sulphate in alkaline soln. reduces potassium ferricyanide to the ferrocyanide on exposure to light. G. A. Barbieri studied the action of ferrous sulphate on **silver ferricyanide**. C. A. L. de Bruyn observed that absolute **methyl alcohol** dissolves the heptahydrate, and that the soln. is unstable; when a few drops of water are added, or when the soln. is warmed, the heptahydrate separates out again. P. Rohland noted that the methyl alcohol soln. reduces cupric to cuprous salts; and G. C. Gibson and co-workers obtained the complex:  $2\text{FeSO}_4 \cdot 3\text{CH}_3\text{OH}$ . E. F. Anthon said that ferrous sulphate is insoluble in **ethyl alcohol** of a sp. gr. less than 0.905; and that alcohol, and sulphuric acid precipitate the salt from its aq. soln. H. Schiff found that 100 parts of a sat. soln. of ferrous sulphate in 40 per cent. alcohol, at  $15^{\circ}$ , contain 0.3 per cent. of the heptahydrate. Methyl, ethyl, **propyl**, *n*- and *iso*-**butyl**, and *iso*-**amyl alcohols** are oxidized by permanganate or hydrogen dioxide in the presence of ferrous salts. A dil. soln. of ethyl alcohol, for instance, in the presence of ferrous sulphate, is oxidized to aldehyde, and in the presence of ferrous oxalate, to acetic acid; and A. G. Doroschewsky and A. J. Bardt showed that ferric salts do not act as catalytic agents in the same way. E. G. Thorin observed that the solubility of **ether** in  $0.5N\text{-FeSO}_4$  is less than in water. W. F. O. de Coninck reported the solubility of ferrous sulphate in **glycol** to be 6 per cent. G. Fuseya and K. Murata found that a mol. of ferrous sulphate unites with 6 mols. of **glycocoll** in aq. soln. J. F. Persoz found that glacial **acetic acid** precipitates ferrous sulphate completely from its aq. soln., and A. W. Davidson also added that the heptahydrate is insoluble in glacial acetic acid. W. Franke observed the formation of complex acetates. W. H. Krug and K. P. McElroy, A. Naumann, and W. Eidmann found that ferrous sulphate is insoluble in **acetone**; and A. Naumann, that it is insoluble in dry **methyl acetate**, or in **ethyl acetate**, dry or sat. with water. S. Hakomori studied the action of citric acid and of oxalic acid on ferrous sulphate; and F. Krauss and K. Berge, the effect of iron salts on the photochemical decomposition of oxalic acid. S. Goldschmidt and co-workers studied the oxidation of **glycollic acid** by hydrogen dioxide. E. Darmois observed that a soln. of ferrous sulphate enhances the dextrorotatory power of **tartaric acid**; and J. H. Long studied the inversion of **cane-sugar** by ferrous sulphate. F. Calzolari found that **hexamethylene tetramine** forms a complex:  $\text{FeSO}_4 \cdot \text{C}_6\text{H}_{12}\text{N}_4 \cdot 9\text{H}_2\text{O}$ ; B. Emmert and H. G. Sottschneider, with **benzoylacetone**; and G. Spacu, with **aniline**, the complex:  $\text{FeSO}_4 \cdot 2\text{C}_6\text{H}_5\text{NH}_2$ . A. Naumann said that ferrous sulphate is insoluble in **pyridine**, but various complex salts have been obtained by W. Lang, F. Reitzenstein, G. Spacu, and R. Weinland and co-workers. F. L. Hahn and co-workers observed that ferrous sulphate forms a complex with  **$\alpha$ -acetaminopyridine**; but E. Borsbach, and F. Blau observed no complex is formed with **quinoline**. F. Blau, H. Freundlich and V. Birstein, L. A. Welo, S. Berkman and H. Zocher, W. Biltz, and W. Manchot observed that a complex is formed with  **$\alpha\alpha'$ -dipyridyl**, but H. Blau obtained no complex with the other dipyridyls— **$\alpha\beta'$ ,  $\beta\beta'$ , or  $\gamma\gamma'$** —F. Blau obtained complexes with  **$\alpha\alpha'$ -dipiperidyl**, and  **$\alpha$ -phenanthroline**, but not with **toluidine**, **naphthylamine**, **phenyldiamine**, or **benzidine**. G. Canneri obtained a complex with **guanidine**; P. C. and N. Ray studied the complex salts formed with **trimethylsulphonium sulphate**, and **triethylsulphonium sulphate**. D. Porret studied the oxidation of ferrous sulphate by **benzoquinone**;

F. M. Jäger and J. A. van Dijk, the complexes with **dipyridyl**. A. M. Malkoff and N. Zvetkova observed that the catalytic activity of ferrous sulphate in the oxidation of **sugars** is retarded by phosphates. L. Soep found that the **aniline dye**, orange II, in 1 per cent. soln., gives short, yellow needles of a complex which produces polarization colours, and which can be utilized as a micro-chemical test. N. N. Biswas and N. R. Dhar studied the chemiluminescence of aniline dyes, hæmatoxylin, etc., in the presence of hydrogen dioxide and ferrous sulphate. E. J. Morgan and J. H. Quastel noted the reduction of **methylene blue** by ferrous sulphate. W. Thomson and F. Lewis studied the action of **india-rubber**.

G. Gore discussed the adsorption of ferrous sulphate from its aq. soln. by powdered **silica**; and R. Riecke, and E. C. Sullivan, the adsorption by **orthoclase**, **clays**, and **china clay**. The iron is thought to be removed as ferric hydroxide whilst the  $\text{SO}_4^{--}$ -ions remain in soln. O. C. Magistad found that in contact with **zeolites** or soil minerals, the  $\text{Fe}^{++}$ -ions in aq. soln. of ferrous sulphate are displaced by  $\text{Ca}^{++}$ -ions, and R. Dollfus observed that a crystal of heptahydrated ferrous sulphate in a soln. of **alkali silicate** produces a column—**silica garden**—which consists of a skin of ferrous silicate with a soln. of ferrous sulphate inside. J. Tünnermann found that when the heptahydrate is triturated with **borax**, a greyish-yellow product is formed, which, when treated with water, yields a greyish-green precipitate.

Soln. of iron salts are reduced to metal by the more electropositive metals like magnesium, zinc, or aluminium. E. Hils studied the action of **silver**. C. Brückner observed that when a mixture of anhydrous ferrous sulphate and powdered **magnesium** is heated in an indifferent gas, the iron is oxidized and sulphur dioxide, thiosulphate, and sulphide are formed; a black sulphide is formed when the mixture is triturated in a mortar. H. Heinrichs also studied the reaction. A. Commaile, and D. Tommasi observed that a neutral aq. soln. of ferrous sulphate reacts with magnesium forming a precipitate of white ferrous hydroxide which in air soon oxidizes to yellow hydrated ferric oxide; hydrogen is also evolved. Z. Roussin observed that with feebly-acidic soln. of the salt, iron is precipitated, and A. Commaile added that the precipitated iron is immediately redissolved. J. Thomsen said that the replacement of iron by magnesium in ferrous sulphate soln. evolves 87.06 Cals. F. Muck studied the action of **zinc** on soln. of ferrous sulphate. H. Heinrichs found that a mixture of ferrous sulphate and powdered **aluminium** begins to form an oxide at about  $600^\circ$ , the reaction proceeds explosively at  $900^\circ$ , and the sulphate is reduced to sulphide. M. J. Salauze studied the reaction. O. Prelinger observed that iron is precipitated by powdered **manganese** from an aq. soln. of ferrous sulphate. C. W. Kastner found that with powdered **iron**, hydrogen sulphide is evolved from an aq. soln. of ferrous sulphate, and a blue subsulphide is formed; P. Sabatier and J. B. Senderens observed that hydrogen is slowly evolved from the aq. soln. J. A. N. Friend and P. C. Barnet said that a soln. of ferrous sulphate acts on iron more slowly than is the case with water.

M. C. Boswell and J. V. Dickson found that when ferrous sulphate is fused with **sodium hydroxide**, hydrogen is given off eq. to the oxygen taken up by the salt. Anhydrous ferrous oxide reacts with **calcium**, **strontium**, and **barium oxides**:  $2\text{FeSO}_4 + \text{CaO} = \text{CaSO}_4 + \text{Fe}_2\text{O}_3 + \text{SO}_2$ , and J. A. Hedvall and J. Heuberger observed that the temp. of reaction are respectively  $444^\circ$ ,  $426^\circ$ , and  $345^\circ$ ; with moist mixtures, ferrous and ferrosic oxides are also formed. J. N. von Fuchs observed no precipitation occurs when soln. of ferrous salts are treated with **calcium carbonate**—*vide* ferric sulphate—but H. C. Sorby, and J. P. Kimball showed that an exchange of bases occurs whereby the calcium is replaced by iron. L. Dieulafoy also found that in the presence of iron, manganese, and zinc salt soln., the iron is precipitated first, and then follow zinc and manganese. F. Thomas found that there is a slow reaction with **cuprous oxide** and soln. of ferrous sulphate:  $\text{Cu}_2\text{O} + 2\text{FeSO}_4 + \text{O}_2 = 2\text{CuSO}_4 + \text{Fe}_2\text{O}_3$ . According to E. Braun, the addition of basic **copper carbonate** to a soln. of ferrous sulphate, produces a dirty green-coloured



precipitate, which, when warmed, turns yellowish-brown, and is thought to be a mixture of cuprous hydroxide and basic ferric sulphate. Cupric hydroxide partially dissolves in a neutral soln. of ferrous sulphate, and the soln. becomes reddish-yellow. W. G. Murray examined the action of 5 per cent. soln. of ferrous sulphate in sea-water and in fresh water, on **oxidized copper ores**—chrysocolla, malachite, and cuprite. In the absence of air, and in a neutral soln., very little copper is dissolved, but with the free access of air, a maximum of 56 per cent. of the total copper dissolved readily, although 98 per cent. was dissolved by acetic acid. The solvent action of ferrous sulphate is attributed to its oxidation to ferric sulphate which behaves as a weak acid, the iron being precipitated as a basic salt by the copper minerals. Malachite is more active than chrysocolla as a precipitant. D. G. Murray, and R. H. Bradford also studied the action of anhydrous ferrous sulphate on copper ores. S. Bodforss found that the  $\text{Fe}^{++}$ -ions in a soln. of ferrous sulphate are readily displaced by  $\text{Ba}^{++}$ -ions but not by  $\text{Be}^{++}$ -ions from **beryllium salts**. I. Sukanuma observed that **aragonite** becomes green by the adsorption of ferrous sulphate from aq. soln., but **calcite** becomes yellow through the formation of a basic sulphate. W. Diesel discussed the adsorption of ammonium ferrous sulphate from its aq. soln. by aragonite, calcite, and **vaterite**. L. Gerstacker found that when the aq. soln. is triturated with **zinc oxide** for half an hour, a dark green colour is produced which gradually darkens. A. Mailhe found that freshly-precipitated **mercuric oxide** gives a mixed precipitate of mercury, mercurous sulphate, and a basic sulphate. F. Bayer extracted the manganese from **manganiferous slags** and ores by heating them under pressure with a soln. of ferrous sulphate.

J. L. Gay Lussac and L. J. Thénard observed that **potassium fluoride** reacts with a soln. of ferrous sulphate forming a white precipitate—probably tetrahydrated ferrous fluoride—which is soluble in a large excess of hydrofluoric acid. A. Ditte showed that when anhydrous ferrous sulphate is melted with **sodium chloride** it does not form crystals of ferric oxide, but with the hydrated sulphate, the crystals are formed. M. von der Ballen reported that when a mixture of the heptahydrate and sodium chloride is gradually heated to redness, hydrogen chloride is evolved and sodium sulphate is formed; but this conclusion was denied by C. F. S. Hahnemann, J. Lieblein, M. Tuhten, and J. C. Wiegand. According to K. H. Oenicke, a mixture of the heptahydrate and sodium chloride, when heated, first gives off water, and a sublimate of ferric chloride is formed; molten sodium chloride was found by G. Rousseau and J. Bernheim to furnish crystals of  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ , and, according to C. F. Rammelsberg, and A. Ditte, crystals of ferric oxide. G. Rousseau and J. Bernheim observed that with molten **potassium chloride**, potassium ferrite is formed, and the proportion of combined water is less the higher is the temp. of formation. F. Kuhlmann found that with molten **calcium chloride** in a closed crucible, magnetic ferrous oxide is formed.

Ferrous sulphate forms complex salts with many of the **metal sulphates**—*vide infra*; and it also acts as a mild reducing agent. M. Randall and C. F. Failey found that in the order of salting out of ions,  $\text{Fe}^{++}$  stands between  $\text{Mg}^{++}$  and  $\text{Zn}^{++}$ . H. Frischer, F. Herrmann, and H. C. Biddle found that a soln. of ferrous sulphate reduces an ammoniacal soln. of a **cupric salt** forming a soln. of a cuprous salt and a precipitate of hydrated ferrous oxide. This reaction offers one mode of preparing a soln. of a cuprous salt for carbon monoxide absorptions in gas analyses. P. Rohland observed that a soln. of ferrous sulphate in methyl alcohol reduces cupric salts to cuprous salts. Ferrous sulphate reduces **silver salts** to the metal:  $\text{Ag}_2\text{SO}_4 + 2\text{FeSO}_4 = 2\text{Ag} + \text{Fe}_2(\text{SO}_4)_3$ ; and also  $3\text{AgNO}_3 + 3\text{FeSO}_4 = 3\text{Ag} + \text{Fe}_2(\text{SO}_4)_3 + \text{Fe}(\text{NO}_3)_3$ . These reactions have been discussed by H. Landolt, A. lo Surdo, W. H. Emmons, A. Heydweiller, Lord Rayleigh, and J. Joly in order to find if there is any appreciable loss of weight during a chemical reaction. L. Pisarschewsky found the equilibrium constant of the reaction:  $\text{Ag}_2\text{SO}_4 + 2\text{FeSO}_4 = \text{Fe}_2(\text{SO}_4)_3 + 2\text{Ag}$ , at  $25^\circ$ , to be  $K = 0.00793$ ; and M. V. Dover, 0.0070. The reaction is sensitive to light, and there is a small disturbance due to the

hydrolysis of the ferric sulphate soln. N. A. Tananaeff gave  $K=0.0018$  at  $0^\circ$ ,  $0.0061$  at  $25^\circ$ , and  $0.0110$  at  $45^\circ$ ; the heat of the reaction is  $7868$  cal. per gram-atom of silver—L. Pissarschewsky gave  $8685$  cal. The reaction was also studied by W. Haehnel, V. Kohlschütter and K. Steck, D. Roberts and F. G. Soper, and R. Luther. The reduction of **gold chloride** by a soln. of ferrous sulphate:  $\text{AuCl}_3 + 3\text{FeSO}_4 = \text{Au} + \text{FeCl}_3 + \text{Fe}_2(\text{SO}_4)_3$ , is utilized in photographic toning. When an acidified soln. of ferrous sulphate is shaken with **mercurous sulphate**, L. W. McCay and W. T. Anderson represented the reaction:  $2\text{FeSO}_4 + \text{Hg}_2\text{SO}_4 \rightleftharpoons \text{Fe}_2(\text{SO}_4)_3 + 2\text{Hg}$ . P. Schwarzkopf found that with **mercuric chloride**, and ferrous sulphate soln. no precipitation occurs for many hours, but if some potassium fluoride be added to the soln., mercurous chloride is precipitated in a few minutes. N. R. Dhar observed that in diffused daylight no reaction occurs in a soln. of ferrous sulphate and mercuric chloride, but in sunlight, there is a slow reduction of the mercuric salt. A mixed soln. of mercuric chloride and ammonium oxalate decomposes in light:  $2\text{HgCl}_2 + (\text{NH}_4)_2\text{C}_2\text{O}_4 = 2\text{HgCl} + 2\text{NH}_4\text{Cl} + 2\text{CO}_2$ . H. C. Winther observed that the sensitiveness of the reaction is dependent on the purity of the salts. Small proportions of iron salts favour the reaction, and it is doubtful if any photochemical action would occur if all traces of iron salts were absent. Again, H. S. Hatfield showed that the liberation of iodine from a soln. of **mercuric iodide** exposed to sunlight does not occur if traces of iron salts be rigorously excluded. T. S. Price showed that a trace of a ferrous salt favours the oxidation of a soln. of **stannous chloride** in air, and the maximum effect is obtained with  $\text{FeCl}_2 : \text{SnCl}_2 = 1 : 100$ . M. Berthelot discussed the thermal value of the reaction between ferrous sulphate and **ferric chloride** in aq. soln., and similarly with **ferric nitrate**. E. M. Walton showed that when heptahydrated ferrous sulphate is mixed with enneahydrated ferric nitrate, or trihydrated ferric chloride, liquefaction occurs.

C. C. Benson found that the rate of oxidation of ferrous sulphate by **chromic acid** is proportional to the second power of the concentration of both the ferrous salt and the acid. The increase in the rate of oxidation by potassium dichromate is proportional to the 1.7th power of its concentration. She also studied the rate of liberation of iodine from potassium iodide by the action of chromic acid in the presence of ferrous salts. The oxidation of ferrous salts by **potassium dichromate** soln. (*q.v.*) is represented by:  $6\text{FeSO}_4 + \text{K}_2\text{Cr}_2\text{O}_7 + 7\text{H}_2\text{SO}_4 = \text{K}_2\text{SO}_4 + \text{Cr}_2(\text{SO}_4)_3 + 3\text{Fe}_2(\text{SO}_4)_3 + 7\text{H}_2\text{O}$ . The reaction is utilized in the volumetric determination of iron; and similarly with the oxidation of ferrous salts by **potassium permanganate** (*q.v.*) in acidic soln.:  $10\text{FeSO}_4 + 2\text{KMnO}_4 + 8\text{H}_2\text{SO}_4 = 5\text{Fe}_2(\text{SO}_4)_3 + \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 8\text{H}_2\text{O}$ . The reaction was studied by J. L. Kassner and co-workers. According to E. Müller and H. Möllering, in the electrometric titration of the reaction between ferrous sulphate and potassium permanganate in sulphuric acid soln.:  $\text{MnO}_4' + 5\text{Fe}'' + 8\text{H}' = \text{Mn}'' + 5\text{Fe}''' + 4\text{H}_2\text{O}$ , the end-potential is  $0.65$  volt if the permanganate is added to the iron soln., and  $0.76$  volt if the ferrous salt be added to the permanganate soln., but in hydrochloric acid soln., the respective values are  $0.67$  volt and  $0.66$  volt. D. R. Hale studied the reaction between ferrous sulphate, potassium permanganate, and sodium arsenite.

The use of ferrous sulphate as a dressing for crops has been discussed by E. J. Russell, A. B. Griffiths, P. M. Delacharbonny, L. Destremx, and H. Boiret and G. Paturel. Beneficial results follow only when an excess of lime is present whereby calcium sulphate is formed; alone, ferrous salts exert a toxic influence on vegetation, and the sterility of badly aerated soils is attributed in part to the presence of ferrous sulphate. Soln. of ferrous sulphate are more or less toxic, and have been used as weed-killers, fungicides, insecticides, etc. D. L. Belding found ferrous sulphate is but slightly toxic to fish. The soln. are astringent, and have been employed as coagulants, and, according to W. L. Brooke, as a primer before painting resinous woods.

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The corrosion figures studied by H. Baumhauer were in agreement with the holohedral, monoclinic symmetry; they are asymmetrical to the single plane of symmetry (010) which is at right-angles to the plane of the paper, and parallel to the longer sides of the page, they also accord with the presence of a diagonal axis of symmetry perpendicular to the plane of asymmetry, *i.e.* parallel to the shorter edges of the page. The optic axial ratios are  $\chi : \psi : \omega = 6.2094 : 8.4172 : 4.1749$ . The optical character is positive; the optic axial angle  $2E$  given by A. Murmann and L. Rotter is  $135^\circ 42'$ ; whilst A. E. H. Tutton gave:

	Li-	C-	Na-	Tl-	Cd-	F-light
$2E$	$133^\circ 8'$	$133^\circ 16'$	$134^\circ 17'$	$135^\circ 12'$	$135^\circ 35'$	$135^\circ 57'$
$2H_a$	$67^\circ 33'$	$67^\circ 30'$	$67^\circ 20'$	$67^\circ 4'$	$66^\circ 55'$	$66^\circ 47'$
$2H_o$	$90^\circ 10'$	$90^\circ 2'$	$89^\circ 33'$	$89^\circ 3'$	$88^\circ 45'$	$88^\circ 29'$
$2V_a$	$76^\circ 16'$	$76^\circ 18'$	$76^\circ 25'$	$76^\circ 28'$	$76^\circ 30'$	$76^\circ 33'$

The apparent angle  $2E$  diminishes about  $4^\circ$  when the temp. is raised from  $10^\circ$  to  $60^\circ$ . W. Hofmann obtained X-radiograms of the salt,  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , and calculated the lattice constants:  $a = 9.28 \text{ \AA}$ ,  $b = 12.58 \text{ \AA}$ ,  $c = 6.22 \text{ \AA}$ , and  $\beta = 10^\circ 50'$ . M. Bentivoglio studied the rate of growth of the crystals.

H. Schiff gave 1.813 for the sp. gr. of the salt; H. G. F. Schröder, 1.886; and L. Playfair and J. P. Joule, 1.848. A. E. H. Tutton gave 1.864 for the sp. gr. at  $20^\circ/4^\circ$ ; and 208.86 for the mol. vol. H. Schiff measured the sp. gr. of aq. soln. of the salt, and G. T. Gerlach recalculated the results, showing that:

$(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	1	5	10	15	20	25	30 per cent.
Specific gravity	1.006	1.030	1.060	1.092	1.124	1.156	1.193

H. Schiff gave for soln. with  $p$  per cent. of  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  at  $16.5^\circ$ :

$p$	26.40	17.60	11.74	8.80	5.87
Sp. gr.	1.1666	1.1083	1.0708	1.0530	1.0354

and he represented the results by:  $\text{Sp. gr.} = 1 + 0.005918p + 0.041083p^2 + 0.061715p^3$ .

I. Traube gave for the volume change which occurs when the salt is dissolved in water at  $16.5^\circ$ : Percentage anhydrous  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$ , 7.245, 10.867, 14.490, and 19.127; with the respective sp. gr., 1.060, 1.092, 1.124, and 1.1666; and the respective vol. changes, 62.1, 63.9, 67.9, and 71.7 units. H. L. Maxwell showed that diffusion experiments indicate that the salt is partially dissociated into its components. C. A. Martius observed the f.p. of soln., and W. A. Kistiakowsky found that the lowerings of the f.p. of soln. of 0.852, 1.798, 3.667, and 7.136 grms. of the hexahydrate in 100 grms. of water were respectively  $0.23^\circ$ ,  $0.44^\circ$ ,  $0.792^\circ$ , and  $1.375^\circ$ , so that the mol. lowerings were respectively 2.895, 3.238, 3.68, and 4.06. E. Rouyer holds that the ebullioscopic observations indicate the existence of the double salt in soln. at  $100^\circ$ . T. Graham found that the heat of soln.,  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O} + \text{Aq.} = -9.8 \text{ Cals.}$  A. Murmann and L. Rotter found the indices of refraction,  $\beta$ , for red-, yellow-, and green-light were respectively 1.487, 1.490, and 1.492. A. E. H. Tutton gave:

	Li-	C-	Na-	Tl-	Cd-	F-	G-light
$\alpha$	1.4839	1.4844	1.4870	1.4896	1.4911	1.4926	1.4971
$\beta$	1.4885	1.4890	1.4915	1.4942	1.4957	1.4972	1.5019
$\gamma$	1.4957	1.4962	1.4989	1.5017	1.5032	1.5047	1.5094

The  $\beta$ -values for any wave-length  $\lambda$  can be represented by  $\beta = 1.4784 + 494204\lambda^{-2} - 885610000000\lambda^{-4} + \dots$ . The  $\alpha$ -values are reproduced if 1.4784 is reduced by 0.0046, and the  $\gamma$ -indices if it be raised by 0.0074. The raising of the temp. from  $10^\circ$  to  $60^\circ$  lowered the  $\alpha$ -values an average of 0.0013, the  $\beta$ -values, 0.0017, and the  $\gamma$ -values 0.0018. The sp. refraction with the  $\mu^2$ -formula for  $\alpha$ ,  $\beta$ , and  $\gamma$  were for the C-ray, respectively 0.1536, 0.1548, and 0.1568, and for the G-ray, respectively 0.1570, 0.1583, and 0.1603; the mol. refractions for the C-ray were 55.61, 56.25, and 57.71 respectively, and for the G-ray respectively 56.78, 57.46, and 58.95. The sp. dispersions,  $\mu_\alpha - \mu_\gamma$ , are accordingly 0.0034, 0.0035, and 0.0035 respectively,

while the mol. dispersions are respectively 1.17, 1.21, and 1.24. For the *C*-ray, and the  $\mu$ -formula, the mol. dispersions are respectively 93.78, 95.05, and 97.94. H. Nisi measured the Raman effect. R. Saxon, and M. Ogoshi studied the electrolysis of aq. soln. of the salt—*vide supra*, the preparation of iron. G. Quincke gave  $44 \times 10^{-6}$  mass unit for the magnetic susceptibility of soln. of ammonium ferrous sulphate at 18°, and O. Liebknecht and A. P. Wills,  $45 \times 10^{-6}$  mass unit at 18°. W. Finke observed for the crystals of the hexahydrate,  $79 \times 10^{-6}$  vol. unit. L. A. Welo measured the magnetic susceptibility of solid and molten ammonium ferric sulphate,  $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , and L. C. Jackson's results for the reciprocal of the mol. magnetic susceptibility at different temp. are summarized in Fig. 645. P. Weiss and C. A. Frankamp studied the susceptibility of aq. soln. For the Curie constant,  $C = \chi(T - \theta)$ , for the solid and liquid states,  $C_s = 4.30$ ;  $C_l = 4.43$ ;  $\theta_s = 0^\circ$ , and  $\theta_l = -173^\circ$ . D. E. Olshevsky studied the orientation of the crystals in a magnetic field; and L. Pauling and M. L. Huggins, the magnetic properties.

Ammonium ferrous sulphate is stable at ordinary temp., and the cold soln. do not readily oxidize, so that it is used for standardizing permanganate soln. C. Baskerville and R. Stevenson found no oxidation occurred when a stream of air was passed for 3 hrs. through an aq. soln. of Mohr's salt acidified with sulphuric acid. They observed no catalytic effects with salts of cobalt, chromium, copper, and manganese—but see ferrous sulphate, above. H. A. von Vogel found that the crystals effloresce a little above 100°, and when heated, they swell up to a white mass, without fusion, and give off water, ammonia, and ammonium sulphate. Sulphuric acid abstracts water from the crystals and makes them opaque. Mohr's salt is less soluble in water than ferrous sulphate. E. Tobler gave for the solubility, *S* grms. of the hexahydrate in 100 grms. of water:

	0°	15°	40°	50°	70°
<i>S</i> . . . . .	12.5	20.0	33.0	40	52

J. Locke found 351 grms. of the anhydrous salt dissolve in a litre of water at 25°. F. A. H. Schreinemakers stated that the salt is soluble in water without decomposition—the aq. soln. at 30° contains 13.13 per cent. of  $\text{FeSO}_4$ , and 11.45 per cent. of ammonium sulphate. M. T. Salazar and E. Moles observed no signs of hydrolysis in the aq. soln. W. Finke found the magnetic susceptibilities in the three crystallographic directions to be for *a*, *b*, and *c*, respectively,  $85.48 \times 10^{-6}$ ,  $75.67 \times 10^{-6}$ , and  $74.90 \times 10^{-6}$  mass unit. S. Kitajima found that the hydrolysis, represented by the acid concentration at 20° to 25°, was:

Concentration	2	5	10	15	20	25	30	50 per cent.
Acidity . . . . .	0.00428	0.00556	0.00707	0.00752	0.00675	0.00669	0.00650	0.00625 <i>N</i>

E. Weitz and H. Müller prepared the amino-analogue of Mohr's salt, namely, **ammonium ferrous aquopentamminosulphate**,  $(\text{NH}_4)_2\text{SO}_4 \cdot [\text{Fe}(\text{H}_2\text{O})(\text{NH}_3)_5]\text{SO}_4$ . Like ferrous sulphate, soln. of this salt readily absorb nitric oxide. W. Eidmann found that the salt is not soluble in acetone. B. V. Nekrasoff studied the absorption of the salt from aq. soln. by charcoal. N. R. Dhar observed that the reaction between silver nitrate and ammonium ferrous sulphate is bimolecular and very rapid at 0° with a small temp. coeff. In due course a state of equilibrium:  $\text{Ag} + \text{Fe}(\text{NO}_3)_3 \rightleftharpoons \text{AgNO}_3 + \text{Fe}(\text{NO}_3)_2$ , is established. The reaction is accelerated by nitric, sulphuric, citric, tartaric, acetic, and carbonic acids, but not by boric acid nor phenol; and it is retarded by manganese salts and potassium nitrate.

According to D. Linck, E. Mitscherlich, D. Brewster, and J. C. G. de Marignac, if a soln. of equimolar proportions of potassium and ferrous sulphates be evaporated at ordinary temp., green crystals of **potassium ferrous sulphate**,  $\text{K}_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ , are formed; and if a soln. of iron filings in one of potassium hydrosulphate be similarly treated, the *hexahydrate* is similarly formed. O. Aschan obtained the salt by the action of a soln. of potassium persulphate on iron. R. M. Caven and J. Ferguson studied the vap. press. of aq. soln., and noted that the hexahydrate

passes into the tetrahydrate which has a dissociation press. of 85.9 mm. at 50°. F. W. Küster and A. Thiel found that when a soln. of equimolar proportions of the two salts crystallizes between 35° and 85°, pale green crystals of the *tetrahydrate*,  $K_2SO_4 \cdot FeSO_4 \cdot 4H_2O$ , are formed, and above 90°, colourless crystals of the *dihydrate*,  $K_2SO_4 \cdot FeSO_4 \cdot 2H_2O$ , are formed. The transition temp. for the hexa- and tetra-hydrates is 30°; for the tetra- and di-hydrates, 87°; and for the hexa- and di-hydrates, 54°, as indicated in Fig. 653. The solubility curves, expressed in terms of the c.c. of 0.1N- $KMnO_4$ , is required for 2 c.c. of the soln. of the double salt, are given in Fig. 653; and when re-calculated to show *S* grms. of  $K_2SO_4 \cdot FeSO_4$  per 100 c.c. of soln., the solubilities of the different hydrates are :

	0.5°	17.2°	40.1°	60.0°	80.0°	90.0°	95.0°
$S \begin{cases} \text{6-hydrate} & . & 19.72 & 27.04 & 39.45 & 46.13 & 48.68 & - \\ \text{4-hydrate} & . & 24.66 & 28.79 & 34.84 & 38.34 & 43.43 & 47.09 \\ \text{2-hydrate} & . & 24.50 & 34.36 & 43.91 & 45.82 & 45.98 & 44.07 \end{cases}$							

J. C. G. de Marignac, and G. Wyrouboff prepared green, tabular crystals of the dihydrate by cooling the soln. rapidly from 60°. The green triclinic crystals have the axial ratios  $a : b : c = 0.7113 : 1 : 0.4501$ , and  $\alpha = 85^\circ 16'$ ,  $\beta = 102^\circ 18'$ , and  $\gamma = 86^\circ 48'$ . The crystals are isomorphous with the corresponding manganous salt. Twinning occurs about the (010)-plane, and the (101)-cleavage is complete, but the (001)-cleavage is incomplete. The optical character is negative, and the optic axial angle  $2E = 96^\circ$ . The sp. gr. is 2.683. The crystals become matt on exposure to air owing to the absorption of moisture.

A. E. H. Tutton obtained green, transparent crystals of the hexahydrate by slow crystallization over conc. sulphuric acid, in vacuo. The crystals are liable to effloresce in vacuo, and, in consequence, should be removed soon after they are formed. J. C. G. de Marignac, H. de Sénarmont, and A. Murmann and L. Rotter examined the crystals of the hexahydrate, and found the monoclinic prisms to be isomorphous with ammonium cobaltous sulphate. According to A. E. H. Tutton, the monoclinic prisms have the axial ratios  $a : b : c = 0.7377 : 1 : 0.5020$ , and  $\beta = 104^\circ 32'$ ; and the topic axial ratios  $\chi : \psi : \omega = 6.0739 : 8.2336 : 4.1332$ . The cleavage parallel to (201) is well defined. The optical character is positive. The optic axial angles are :

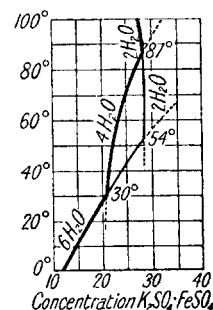


FIG. 653.—Solubility of Potassium Ferrous Sulphate.

	Li-	C-	Na-	Tl-	F-light
$2H_{\alpha}$ . . .	66° 52'	66° 52'	66° 55'	66° 57'	67° 2'
$2H_{\beta}$ . . .	112° 38'	112° 39'	112° 27'	112° 17'	112° 2'
$2V_{\alpha}$ . . .	67° 1'	67° 2'	67° 7'	67° 12'	67° 19'
$2E$ . . .	109° 37'	109° 41'	110° 10'	110° 35'	111° 51'

Observations were also made by A. Murmann and L. Rotter, and H. Topsøe and C. Christiansen; the latter gave  $2V = 67^\circ 78'$ , and  $2E = 110^\circ 32'$  for the *D*-line. A. E. H. Tutton observed that the apparent axial angle in air is increased about 2° for each rise of temp. up to 50°, at which temp., the crystals become opaque. H. Schiff gave 2.18 for the sp. gr. of the hexahydrate, L. Playfair and J. P. Joule gave 2.202. H. G. F. Schröder gave 3.042 for the sp. gr. of the anhydrous salt, whilst A. E. H. Tutton found 2.1694 at 20°/4° for the sp. gr., and 200.09 for the mol. vol. R. M. Caven and J. Ferguson found that the dissociation press. of potassium ferrous sulphate, *p* mm., is :

	25.1°	39.0°	50.7°	61.7°	71.5°
<i>p</i> . . .	21.0	48.3	89.1	148.6	228.9

and the data can be represented by  $\log p = 6.768 - 866.5T^{-1} - 244400T^{-2}$ . The heat of hydration of the tetrahydrate per mol. of water vapour is 10.4 Cals. T. Graham

found that the heat of soln. is  $-10.7$  Cals. A. E. H. Tutton gave for the mean refractive indices :

	Li-	C-	Na-	Tl-	F-	G-light
$\alpha$ . . .	1.4731	1.4735	1.4759	1.4782	1.4811	1.4852
$\beta$ . . .	1.4795	1.4799	1.4821	1.4847	1.4877	1.4920
$\gamma$ . . .	1.4941	1.4945	1.4969	1.4995	1.5028	1.5071

H. Topsøe and C. Christiansen found for C-, Na-, and F-light, the respective values  $\alpha=1.4751$ ,  $1.4775$ , and  $1.4833$ ;  $\beta=1.4806$ ,  $1.4832$ , and  $1.4890$ ; and  $\gamma=1.4947$ ,  $1.4973$ , and  $1.5041$ . A. Murmann and L. Rotter gave  $\beta=1.478$  for red-light;  $1.480$  for yellow-light;  $1.484$  for green light; and  $1.489$  for violet-light. A. E. H. Tutton represented the vacuum values of  $\beta$ , for light of wave-length  $\lambda$  as far as F, by  $\beta=1.4728+266439\lambda^{-2}+243790000000\lambda^{-4}+\dots$ ; and if  $1.4728$  be altered to  $1.4664$  it represents the value of  $\alpha$ , and if changed to  $1.4875$ , values of  $\gamma$ . The indices at  $55^\circ$  were about  $0.0010$  lower than at ordinary temp. The sp. refractions by the  $\mu^2$ -formula for  $\alpha$ ,  $\beta$ , and  $\gamma$  for the C-line are respectively  $0.1296$ ,  $0.1301$ , and  $0.1344$ , and for the G-line, respectively  $0.1323$ ,  $0.1339$ , and  $0.1373$ ; the corresponding mol. refractions for the C-line are respectively  $56.22$ ,  $56.87$ , and  $58.34$ , and for the G-line respectively  $57.41$ ,  $58.09$ , and  $59.60$ . The sp. dispersions  $\mu_G-\mu_C$ , are respectively  $0.0027$ ,  $0.0029$ , and  $0.0029$ , with the corresponding mol. dispersions,  $1.19$ ,  $1.22$ , and  $1.26$  respectively. The mol. refractions by the  $\mu$ -formula, and the C-line are  $94.82$ ,  $96.10$ , and  $99.03$  respectively for  $\alpha$ ,  $\beta$ , and  $\gamma$ . These values are almost constant for the range of temp. in which the salt can exist. I. I. Rabi observed that the crystals are paramagnetic; and K. S. Krishnan and co-workers studied the magnetic properties. Y. Ono studied the oxidation of a mixed soln. of ammonium ferrous sulphate and ammonium oxalate by potassium permanganate. S. Miyamoto studied the effect of hydrogen and the silent discharge on the salt.

H. G. F. Schröder gave  $3.042$  for the sp. gr. of the anhydrous salt obtained by fusing together the correct proportions of the component salts. F. Ephraim and P. Wagner discussed the mol. vol. J. C. G. de Marignac said that the crystals of the hexahydrate form potassium sulphate and ferric oxide when heated in air. E. Tobler gave for the solubility  $S$  grms. of the anhydrous salt per  $100$  grms. of water—*vide supra* :

	$0^\circ$	$10^\circ$	$14.5^\circ$	$16^\circ$	$25^\circ$	$35^\circ$	$40^\circ$	$55^\circ$	$65^\circ$	$70^\circ$
$S$ . . .	19.6	24.5	29.1	30.9	36.5	41	45	56.1	59.3	64.2

A. E. H. Tutton prepared pale green, transparent crystals of **rubidium ferrous sulphate**,  $\text{Rb}_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ , by the method employed for the potassium salt. The monoclinic crystals have the axial ratios  $a:b:c=0.7377:1:0.5004$ , and  $\beta=105^\circ 44'$ . Observations were also made by F. L. Perrot. A. E. H. Tutton gave for the topic axial ratios  $\chi:\psi:\omega=6.1832:8.2817:4.1942$ . The  $(201)$ -cleavage is perfect. The optical character is positive. The optic axial angles :

	Li-	C-	Na-	Tl-	F-light
$2H_a$ . . .	$73^\circ 5'$	$73^\circ 3'$	$72^\circ 56'$	$72^\circ 48'$	$72^\circ 35'$
$2H_o$ . . .	$105^\circ 54'$	$105^\circ 50'$	$105^\circ 41'$	$105^\circ 32'$	$105^\circ 21'$
$2V_a$ . . .	$73^\circ 24'$	$73^\circ 23'$	$73^\circ 21'$	$73^\circ 18'$	$73^\circ 13'$
$2E$ . . .	$124^\circ 42'$	$124^\circ 49'$	$125^\circ 12'$	$125^\circ 41'$	$126^\circ 16'$

A. E. H. Tutton said that the optic axial angle increases about  $1^\circ$  per  $50^\circ$  rise of temp. F. L. Perrot gave  $2.51$  for the sp. gr. at  $15^\circ$ , and A. E. H. Tutton,  $2.516$  at  $20^\circ/4^\circ$ , and  $209.22$  for the mol. vol. F. Ephraim and P. Wagner discussed the mol. vol. A. E. H. Tutton found that the mean refractive indices are :

	Li-	C-	Na-	Tl-	F-	G-light
$\alpha$ . . .	1.4789	1.4793	1.4815	1.4839	1.4870	1.4916
$\beta$ . . .	1.4847	1.4851	1.4874	1.4898	1.4929	1.4973
$\gamma$ . . .	1.4949	1.4953	1.4977	1.5003	1.5034	1.5080

F. L. Perrot gave a set of values from which, for the D-line,  $\alpha=1.4812$ ,  $\beta=1.4870$ ,

and  $\gamma=1.4978$ . A. E. H. Tutton gave for  $\beta$  for any wave-length  $\lambda$ , as far as  $F$ ,  $\beta=1.4747+508396\lambda^{-2}-186310000000\lambda^{-4}+\dots$ , and if 1.4747 be diminished by 0.0059, the  $\alpha$ -indices are reproduced, and if it be increased by 0.0103, the  $\gamma$ -indices. At  $60^\circ$ , the indices are about 0.0014 lower than they are at ordinary temp. The sp. refractions, with the  $\mu^2$ -formula for  $\alpha$ ,  $\beta$ , and  $\gamma$ , with the  $C$ -line, are respectively 0.1128, 0.1140, and 0.1160, and with the  $G$ -line, respectively 0.1153, 0.1164, and 0.1186; the corresponding mol. refractions with the  $C$ -line, respectively 59.40, 60.02, and 61.09; and with the  $G$ -line, respectively 60.70, 61.30, and 62.41. The sp. dispersions  $\mu_G-\mu_C$ , for  $\alpha$ ,  $\beta$ , and  $\gamma$ , are respectively 0.0025, 0.0024, and 0.0026, and the mol. dispersions respectively 1.30, 1.28, and 1.32. The mol. refractions, by the  $\mu$ -formula, are respectively 100.36, 101.58, and 103.71. J. Locke found that 0.579 mol or 242 grms. of the anhydrous salt dissolve in a litre of water at  $25^\circ$ . R. M. Caven and J. Ferguson studied the vap. press. of aq. soln.

A. E. H. Tutton also prepared pale green, transparent crystals of **caesium ferrous sulphate**,  $\text{Cs}_2\text{SO}_4\cdot\text{FeSO}_4\cdot 6\text{H}_2\text{O}$ , by the method used for the potassium salt. The monoclinic crystals have the axial ratios  $a:b:c=0.7261:1:0.4953$ , and  $\beta=106^\circ 52'$ ; while the topic axial ratios  $\chi:\psi:\omega=6.2799:8.6487:4.2837$ . The  $(20\bar{1})$ -cleavage is complete. The optical character is positive; and the optic axial angles are:

	Li-	C-	Na-	Tl-	F-light
$2H_a$	$67^\circ 10'$	$67^\circ 5'$	$66^\circ 43'$	$66^\circ 16'$	$65^\circ 43'$
$2H_o$	$92^\circ 12'$	$92^\circ 7'$	$91^\circ 50'$	$91^\circ 30'$	$91^\circ 3'$
$2V_a$	$75^\circ 2'$	$75^\circ 0'$	$74^\circ 51'$	$74^\circ 42'$	$74^\circ 31'$

$2E$  for the Na-line is  $132^\circ 47'$ . There is a decrease of about  $1\frac{1}{2}^\circ$  for a rise of  $50^\circ$  in temp. The sp. gr. at  $20^\circ/4^\circ$  is 2.7909, and the mol. vol. 222.64. F. Ephraim and P. Wagner discussed the mol. vol. A. E. H. Tutton found that the indices of refraction are:

	Li-	C-	Na-	Tl-	F-	G-light
$\alpha$	1.4976	1.4980	1.5003	1.5028	1.5061	1.5105
$\beta$	1.5007	1.5011	1.5035	1.5061	1.5093	1.5137
$\gamma$	1.5065	1.5069	1.5094	1.5121	1.5153	1.5198

The value of the  $\beta$ -index for any wave-length  $\lambda$  as far as  $F$  is  $\beta=1.4911+462915\lambda^{-2}-645800000000\lambda^{-4}+\dots$ , and if 1.4911 is diminished by 0.0032, the formula represents the  $\alpha$ -indices, and if increased by 0.0059, the  $\gamma$ -indices. At  $70^\circ$ , the indices are lower by about 0.0017 than they are at ordinary temp. The sp. refractions with the  $\mu^2$ -formula, for  $\alpha$ ,  $\beta$ , and  $\gamma$ , with the  $C$ -line are respectively 0.1051, 0.1057, and 0.1067, and with the  $G$ -line, 0.1073, 0.1079, and 0.1090; whilst the corresponding mol. refractions for the  $C$ -line are respectively 65.31, 65.65, and 66.29; and for the  $G$ -line, 66.69, 67.04, and 67.71. The sp. dispersions,  $\mu_G-\mu_C$ , are respectively 0.0022, 0.0022, and 0.0023, and the mol. dispersions, respectively 1.38, 1.39, and 1.42. The mol. refractions by the  $\mu$ -formula are respectively 111.01, 111.70, and 112.90. J. Locke found that 1.967 mols or 1011 grms. of the anhydrous salt dissolve in a litre of water at  $25^\circ$ . This high solubility is in marked contrast with the low solubility of ferric caesium-alum. R. M. Caven and J. Ferguson studied the vap. press. of aq. soln.

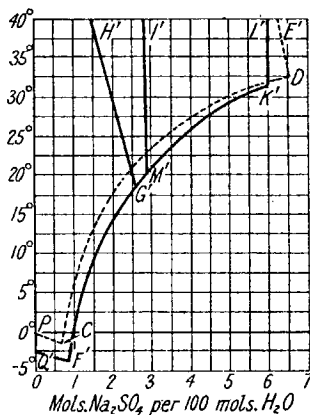
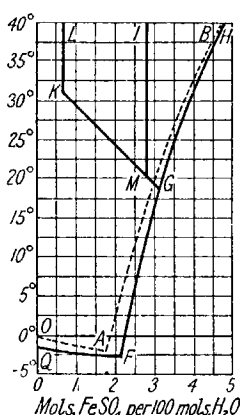
A. E. H. Tutton compared the axial angles of the ammonium, potassium, rubidium, and caesium salts, and observed that if the first member be excepted, the axial angle,  $\beta$ , steadily increases with the mol. wt., while the axial ratios of the first three salts are very close, those of the caesium salt are exceptional. Similarly with the sp. gr. and mol. vol. By interchanging rubidium for ammonium, very little change occurs in the mol. vol. in spite of the fact that two atoms of rubidium are replaced by the ten nitrogen and hydrogen atoms of ammonium. The sp. gr. increase with the mol. wt., and likewise also the mol. vols. if ammonium be excepted.

F. A. H. Schreinemakers did not observe the formation of a **lithium ferrous sulphate** in his study of the ternary system:  $\text{FeSO}_4\text{-Li}_2\text{SO}_4\text{-H}_2\text{O}$ , at  $30^\circ$ , Fig. 652. The solubilities in percentages by weight are:



FeSO <sub>4</sub>	.	.	24.87	22.45	16.18	16.04	15.39	12.68	5.32	0
Li <sub>2</sub> SO <sub>4</sub>	.	.	0	4.00	16.52	16.49	16.80	18.31	22.15	25.1
Solid phase			FeSO <sub>4</sub> ·7H <sub>2</sub> O		FeSO <sub>4</sub> ·7H <sub>2</sub> O + Li <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O		Li <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O			

F. A. H. Schreinemakers also studied the quaternary system: FeSO<sub>4</sub>-Li<sub>2</sub>SO<sub>4</sub>-(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O at 30°, and found the ranges of stability for the complex salts Li<sub>2</sub>SO<sub>4</sub>·(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, and FeSO<sub>4</sub>·(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>·6H<sub>2</sub>O. J. C. G. de Marignac obtained pale green crystals of **sodium ferrous sulphate**, Na<sub>2</sub>SO<sub>4</sub>·FeSO<sub>4</sub>·4H<sub>2</sub>O, by evaporation of a soln. of equimolar proportions of the component salts at 35° or over. O. Aschan obtained the salt by the action of a soln. of sodium persulphate on iron. The monoclinic prisms have the axial ratios  $a:b:c=1.3494:1:0.6693$ , and  $\beta=100^\circ 27'$ . J. Koppel's observations on the system: Na<sub>2</sub>SO<sub>4</sub>-FeSO<sub>4</sub>-H<sub>2</sub>O are summarized in Figs. 654 and 655. Corresponding soln. are designated with similar letters in both diagrams, those without a dash refer to ferrous sulphate soln., and those with a dash to soln. of sodium sulphate. The curves *FG*, and *F'G'* refer



FIGS. 654 and 655.—The Mutual Solubilities of Sodium and Ferrous Sulphates.

to the solubilities of mixtures of the component sulphates: *MI* and *M'I'*, to the solubility of the complex salt Na<sub>2</sub>SO<sub>4</sub>·FeSO<sub>4</sub>·4H<sub>2</sub>O; *GH* and *G'H'*, to that of a mixture of the complex salt and FeSO<sub>4</sub>·7H<sub>2</sub>O; *GKL* and *G'K'L'*, to that of a mixture of the complex salt and Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O or Na<sub>2</sub>SO<sub>4</sub>; *OAB*, to the solubility of ferrous sulphate; *PCDE*, to the solubility of sodium sulphate; *A*, to the eutectic of FeSO<sub>4</sub>·7H<sub>2</sub>O and water; and *C*, to the eutectic of Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O and water. The temp. of formation of the complex salt, Na<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O, is 18.5°; in the presence of the double salt, the transformation Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O ⇌ Na<sub>2</sub>SO<sub>4</sub> + 10H<sub>2</sub>O occurs at 31.4°. The eutectic of FeSO<sub>4</sub>·7H<sub>2</sub>O and ice occurs at -2°; and that of FeSO<sub>4</sub>·7H<sub>2</sub>O and Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O at -3°. The transformation equation at *G*, or *G'*, is Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O + FeSO<sub>4</sub>·7H<sub>2</sub>O = 0.56Na<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O + 0.077Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O + solution 0.14(100H<sub>2</sub>O + 2.6Na<sub>2</sub>SO<sub>4</sub> + 3.15FeSO<sub>4</sub>).

A. and H. Benrath examined the system Na<sub>2</sub>SO<sub>4</sub>-FeSO<sub>4</sub>-H<sub>2</sub>O at 97°. The following is a selection from the results for the solution, where the proportions of ferrous and sodium sulphates are expressed in percentages by weight;  $x$  denotes the mol. proportion of FeSO<sub>4</sub> in the mixture, and  $M$ , the number of mols. of water per mol. of salt:

FeSO <sub>4</sub>	.	0	1.46	2.35	3.94	6.54	7.32	11.20	18.47	19.57	per cent.
Na <sub>2</sub> SO <sub>4</sub>	.	30.50	29.09	28.11	27.17	24.91	22.87	19.22	1.92	0	
$x$	.	0	4.48	7.24	11.93	19.60	23.00	35.28	89.90	100.00	
$M$	.	18.00	18.00	18.11	17.62	17.45	18.53	18.51	32.74	34.70	
Solid phases:											
		Na <sub>2</sub> SO <sub>4</sub>		FeSO <sub>4</sub> ·3Na <sub>2</sub> SO <sub>4</sub>		Na <sub>2</sub> SO <sub>4</sub> ·FeSO <sub>4</sub> ·2H <sub>2</sub> O		FeSO <sub>4</sub> ·H <sub>2</sub> O			

The results are summarized in Fig. 656. At this temp. the *tetrahydrate* indicated above does not appear, but there is the *dihydrate*,  $\text{Na}_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 2\text{H}_2\text{O}$ , as well as **sodium ferrous tetrasulphate**,  $3\text{Na}_2\text{SO}_4 \cdot \text{FeSO}_4$ .

The pseudonymous writer, Basil Valentine, in his *Lectures Testament* (Strassburg, 1651), referred to a mixed vitriol of copper and iron; and in 1715, J. F. Henckel<sup>2</sup> also showed that intimate mixtures of the two vitriols are formed when they crystallize together. J. B. L. Romé de l'Isle, also, referred to what he called *les vitriols mixtes*, and showed that the intimate mixture of iron and copper vitriols furnishes *cubes rhomboïdaux*. The mixed vitriols were also discussed by J. J. Bernhardt, F. S. Beudant, H. D. A. Ficinus, F. Heeren, W. H. Wollaston, A. J. M. Brochant de Villiers, A. Arzruni, E. Mitscherlich, A. G. Monnet, N. Leblanc, E. Wohlwill, L. de Boisbaudran, etc. The isomorphous mixture is sometimes formed when the vitriol has been made from cupriferos pyrites. E. Mitscherlich showed that those crystals which have the form of green vitriol are heptahydrated; and F. S. Beudant said that the crystals have the form of heptahydrated ferrous sulphate if they contain 9 per cent. or more of the salt; and if less than 9 per cent., the crystals resemble those of pentahydrated cupric sulphate. Their colour inclines to green or blue in proportion as the iron or copper predominates. J. W. Retgers observed that soln. of pentahydrated cupric sulphate and heptahydrated ferrous sulphate furnish two kinds of solid soln. He obtained a continuous isomorphous series of monoclinic crystals with from 0 to 53.17 per cent. of heptahydrated cupric sulphate and 46.83 to 100 per cent. of heptahydrated ferrous sulphate; and isomorphous mixtures of triclinic crystals with 94.88 to 100 per cent. of pentahydrated cupric sulphate and 5.12 to 0 per cent. of pentahydrated ferrous sulphate. This subject was also discussed by W. Stortenbeker; and cupriferos melanterite from Cyprus was described by M. H. Hey.

Solid soln. of copper and ferrous sulphates occur in nature in bright blue concretionary or stalactitic forms, and occasionally in crystals. F. Pisani observed one in a copper mine in Turkey; and C. Hintze, one in the mines near Massa Marittima, Tuscany; H. F. Collins, in the Rio Tinto mines of Spain where it was formed by the oxidation of cupriferos pyrites; and W. T. Schaller, near Leona Heights, and at Gonzales, California. There is no definite relation between the proportion of the iron and copper. W. T. Schaller, H. F. Collins, W. F. Hillebrand, F. R. van Horn, H. Leitmeier, C. Hintze, and W. Herz, reported analyses of the mineral. J. W. Retgers said that the mineral is not homogeneous, and the analyses must be represented by the formula:  $(\text{Fe,Cu})\text{SO}_4 \cdot 7\text{H}_2\text{O}$ . A. Descloizeaux called it *cuproferrite*; M. Adam, *cyanoferrite*; and G. A. Kenngott, **pisanite**. G. Vavrinec analyzed the mineral. A. Descloizeaux found that the monoclinic crystals have the axial ratios  $a:b:c=1.1609:1:1.5110$ , and  $\beta=74^\circ 38\frac{1}{2}'$ ; the (001)-cleavage is easy. The optical character is positive; and C. Hintze gave for the optical axial angles in red-light,  $2H_a=86^\circ 8'$ , and  $2H_o=94^\circ 25'$ ; in yellow-light,  $2H_a=85^\circ 52'$ , and  $2H_o=94^\circ 59'$ ; and in green light,  $2H_a=65^\circ 3'$ , and  $2H_o=95^\circ 31'$ . W. Herz reported a green, bluish-green, or blue salt from the Salvador Mine, Calama, Chile, and he called it **salvadorite**. Its composition is like that of pisanite, but its optical orientation is different. The monoclinic crystals occur in aggregates of rough prismatic crystals. Twinning occurs. The (010)-cleavage is perfect. E. S. Larsen gave for the monoclinic crystals of pisanite,  $\alpha=1.472$ ,  $\beta=1.479$ , and  $\gamma=1.487$ . E. S. Larsen and M. L. Glenn observed the occurrence of pale greenish-blue monoclinic crystals forming columnar masses consisting of microscopic rods not sensibly pleochroic. They called the mineral **copper-melanterite**,  $(\text{Zn,Cu,Fe})\text{SO}_4 \cdot 7\text{H}_2\text{O}$ . The biaxial crystals have the optic axial angle  $2V$  nearly

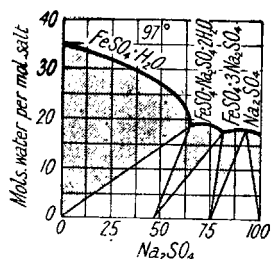


FIG. 656.—Equilibrium in the System:  $\text{Na}_2\text{SO}_4\text{--FeSO}_4\text{--H}_2\text{O}$ , at  $97^\circ$ .

100°; the optical character is negative; the sp. gr. is 2.02; the hardness is 2.0; and the refractive indices,  $\alpha=1.479$ ,  $\beta=1.483$ , and  $\gamma=1.488$ . They also observed pale green, triclinic crystals of **iron-chalcanthite**,  $(\text{Fe,Cu})\text{SO}_4 \cdot 5\text{H}_2\text{O}$ . The optical character was negative; the optic axial angle  $2V$ , moderately large; the indices of refraction,  $\alpha=1.517$ ,  $\beta=1.536$ , and  $\gamma=1.543$ ; and the dispersion,  $\gamma-\alpha=0.026$ . E. S. Larsen gave 1.9 for the sp. gr. of pisanite, and H. Leitmeier, 1.950.

It is doubtful if **copper ferrous sulphate** as a chemical individual has been prepared. The products behave like solid soln. A. Étard treated a conc. soln. of copper and ferrous sulphates with a large excess of conc. sulphuric acid in the cold, and obtained small, brick-red crystals approximating  $\text{CuSO}_4 \cdot \text{FeSO}_4 \cdot 2\text{H}_2\text{O}$ . When heated they become violet, and lose their combined water. A. Scott mixed 100 grms. of pentahydrated ferrous sulphate, 90 grms. of pentahydrated copper sulphate, and 200 c.c. of water, and added 170 c.c. of conc. sulphuric acid to the filtered soln. The homogeneous crystals were yellowish-brown, and approximated in composition  $\text{CuSO}_4 \cdot 2\text{FeSO}_4 \cdot 3\text{H}_2\text{O}$ . They were non-hygroscopic under ordinary conditions, but water is absorbed from a warm, humid atmosphere. When the crystals are gently heated, they become chocolate-brown and then mauve. The original colour is restored on exposing the crystals to air. C. von Hauer obtained crystals approximating  $\text{CuSO}_4 \cdot 2\text{FeSO}_4 \cdot 21\text{H}_2\text{O}$ , isomorphous with the corresponding cobalt salt. Some varieties of pisanite were found by W. T. Schaller to have this formula. J. Lefort, and J. Nicklès obtained crystals of  $\text{CuSO}_4 \cdot 3\text{FeSO}_4 \cdot 28\text{H}_2\text{O}$  from a soln. containing these proportions of the component salts. They lose water in air, and over conc. sulphuric acid. They begin to melt in their water of crystallization at 100°, and lose 24 mols. of water at 100° to 120°, and the remainder at 300°. 100 parts of water at 7° dissolve 75 parts of the salt, and more is dissolved at a higher temp. G. Agde and H. Barkholt showed that mixed soln. of the two salts do not furnish triclinic solid soln. consisting of 95 to 100 per cent.  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and 5 to 0 per cent.  $\text{FeSO}_4 \cdot 5\text{H}_2\text{O}$ ; the solid phase in equilibrium with a soln. containing 35 to 40 per cent. of copper sulphate and less than 6 per cent. of ferrous sulphate is pure  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . From soln. richer in iron, the monoclinic solid soln. containing 61 to 62 per cent.  $\text{CuSO}_4 \cdot 7\text{H}_2\text{O}$ , crystallizes out on evaporation or cooling. On the ferrous sulphate side a continuous series of monoclinic solid soln. containing  $\text{CuSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  in molecular ratios varying from 1 : 50 to 1 : 0.66 crystallizes out. The latter is identical with the double salt described by F. Pisani as  $3\text{CuSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $2\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ; but it appears not to be a true double salt, but simply the limiting solid soln. Re-crystallization of mixed crystals of any composition invariably yields crystals poorer in copper sulphate and a correspondingly richer mother-liquor. F. K. Cameron and H. D. Crockford measured the mutual solubilities of the two sulphates in water and obtained for the weights of the respective salts in 100 grms. of water :

25°	{	$\text{CuSO}_4$	.	.	22.61	18.37	15.76	11.18	8.48	3.03
		$\text{FeSO}_4$	.	.	13.08	13.55	16.04	19.82	22.28	26.61
30°	{	$\text{CuSO}_4$	.	.	23.53	21.56	20.54	18.95	16.02	
		$\text{FeSO}_4$	.	.	3.13	6.86	17.16	19.61	22.75	
40°	{	$\text{CuSO}_4$	.	.	31.68	28.78	21.92	16.89	10.30	3.71
		$\text{FeSO}_4$	.	.	22.14	72.47	20.94	25.07	31.46	37.09

The results are plotted in Fig. 657—*vide* Fig. 640. The presence of sulphuric acid lowers the solubility of either salt. For various mixtures of the two salts in sulphuric acid and water, the composition of the solid phases in equilibrium with the soln. corresponds with mixtures of pentahydrated cupric sulphate,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , and of acid ferrous sulphates,  $\text{FeSO}_4 \cdot n\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ . E. B. Eckel, W. Schrenzlowa, and B. Haber-Chuwis studied solid soln. of the two sulphates. The complex  $3(\text{CuSO}_4 \cdot 7\text{H}_2\text{O}) + 2(\text{FeSO}_4 \cdot 7\text{H}_2\text{O})$ , described by F. Pisani as occurring in a Turkish mine in the form of stalactites, was not observed.

The colour of A. Étard's, and A. Scott's preparations is curious if the salts are

really solid soln. Monohydrated ferrous sulphate is white, and that of copper sulphate, pale blue. A. J. Allmand found that the colour of the homogeneous solid soln. increases in depth from both ends of the series reaching a maximum where 18 per cent. Fe and 16 per cent. of Cu are present. A very small quantity of ferric iron is always present, being formed as an impurity in virtue of the reaction:  $2\text{CuSO}_4 + 2\text{FeSO}_4 = \text{Cu}_2\text{SO}_4 + \text{Fe}_2(\text{SO}_4)_3$ ; the salts are always slightly basic even when formed in acidic soln. The deficiency of " $\text{SO}_4$ " is attributed to the hydrolysis of the ferric sulphate. Cupric sulphate dissolves in solid ferrous sulphate in the form of normal molecules up to about 75 per cent., and thereafter polymerization occurs. A. J. Allmand inferred that the colour is not due to ferric salts or to cuprous salts, but rather to an oscillation of electrons due to the presence of metals in different stages of oxidation. Ferric ferrocyanide and ferrous ferricyanide are also coloured, and similar conditions there prevail.

H. Vohl obtained pale blue, monoclinic columns and plates of **ammonium copper ferrous sulphate**,  $2(\text{NH}_4)_2\text{SO}_4 \cdot \text{CuSO}_4 \cdot \text{FeSO}_4 \cdot 12\text{H}_2\text{O}$ , by crystallization from a soln. of the component salts; he also obtained, in a similar way, crystals of **potassium copper ferrous sulphate**,  $\text{K}_2\text{SO}_4 \cdot \text{CuSO}_4 \cdot \text{FeSO}_4 \cdot 12\text{H}_2\text{O}$ . The products, however, are isomorphous mixtures or solid soln.

G. Klatzo<sup>3</sup> reported that when a soln. of equimolar parts of beryllium and ferrous sulphates in water, acidified with sulphuric acid, is evaporated, pale blue, monoclinic crystals of **beryllium ferrous sulphate**,  $\text{BeSO}_4 \cdot 2\text{FeSO}_4 \cdot 35\text{H}_2\text{O}$ , are first deposited, and afterwards colourless monoclinic crystals of  $3\text{BeSO}_4 \cdot \text{FeSO}_4 \cdot 28\text{H}_2\text{O}$ . P. B. Sarkar and N. Ray prepared **ammonium beryllium ferrous fluosulphate**,  $(\text{NH}_4)_2\text{BeF}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ . H. Schiff prepared **magnesium ferrous sulphate**,  $\text{MgSO}_4 \cdot \text{FeSO}_4 \cdot 14\text{H}_2\text{O}$ , by evaporation from a mixed soln. of equimolar proportions of the constituent salts. The greenish-white crystals have a sp. gr. 1.733. The salt was studied by T. V. Barker, and observations on the solid soln. of the two salts were discussed in connection with the crystals of ferrous sulphate. H. Vohl also found that crystals of **potassium magnesium ferrous sulphate**,  $2\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot \text{FeSO}_4 \cdot 12\text{H}_2\text{O}$ , are deposited from a mixed soln. of the three component salts; and similarly with **ammonium magnesium ferrous sulphate**,  $2(\text{NH}_4)_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot \text{FeSO}_4 \cdot 12\text{H}_2\text{O}$ , and with  $4(\text{NH}_4)_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 3\text{FeSO}_4 \cdot 24\text{H}_2\text{O}$ . These products are probably isomorphous mixtures. The solid soln. of the heptahydrates of magnesium and ferrous sulphates were studied by C. F. Rammeisberg. J. W. Retgers showed that with mixed soln. of the heptahydrates of magnesium and ferrous sulphates, the almost colourless crystals with 0 to 18.78 per cent. of the ferrous salt, and 100 to 81.22 per cent. of the magnesium salt, are rhombic; and the pale green crystals with 45.93 to 100 per cent. of the ferrous salt, and 54.07 to 0 per cent. of the magnesium salt, are monoclinic. The sp. gr. and sp. vol. of some of the solid soln., Fig. 658, were found to be:

$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	5.72	13.99	21.08	31.16	41.02	54.07	81.22	88.16	94.16%
Sp. gr.	1.884	1.867	1.847	1.827	1.807	1.781	1.711	1.697	1.687
Sp. vol.	0.5308	0.5356	0.5415	0.5474	0.5533	0.5613	0.5845	0.5891	0.5927

Monoclinic

Rhombic

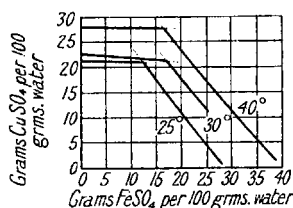


FIG. 657.—Mutual Solubilities of Cupric and Ferrous Sulphates in Water.

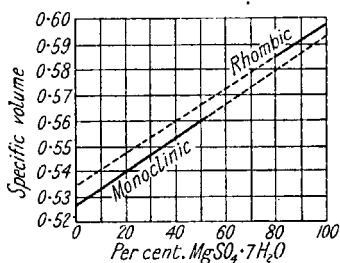


FIG. 658.—Specific Volumes of Isomorphous Mixtures of Ferrous and Magnesium Sulphates.

A. Scott obtained crystals of **zinc ferrous sulphate**,  $\text{ZnSO}_4 \cdot \text{FeSO}_4 \cdot \text{H}_2\text{O}$ , by

adding conc. sulphuric acid to a conc. soln. of the mixed component sulphates. J. W. Retgers found that soln. of the two salts furnish isomorphous mixtures—the colourless crystals with 0 to 10·87 per cent. of heptahydrated ferrous sulphate, and 100 to 89·13 per cent. of heptahydrated zinc sulphate, are rhombic; and the colourless to pale green crystals with 25·11 to 100 per cent. of heptahydrated ferrous sulphate, and 74·89 to 0 per cent. of heptahydrated zinc sulphate, are monoclinic. The monoclinic crystals of the zinc vitriols were studied by A. Arzruni; and A. Murmann studied the crystals of the solid soln. L. Rolla and G. Ansaldi found that the equilibrium temp. of the solid soln.,  $\text{ZnSO}_4 \cdot n\text{FeSO}_4 \cdot 7(1+n)\text{H}_2\text{O}$ , is  $16\cdot4^\circ$ , and that each constituent dissociated independently of the other. C. Andreatta described the *octodecahydrate* of **zinc ferrous trisulphate**,  $\text{Zn}_2\text{Fe}(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ , which occurred as a mineral in crusts in the artificial caves of the mines at Raibl, Trentino. The mineral was called **bianchite**—after A. Bianchi. It occurs in minute, white, microscopic needles resembling goslarite. The crystals are monoclinic. This agrees with the X-radiograms. The optical character is negative; the optical axial angle is small,  $2V=10^\circ$ . The dispersion is weak. The *dihydrate*,  $\text{Zn}_2\text{Fe}(\text{SO}_4)_3 \cdot 2\text{H}_2\text{O}$ , is formed at  $150^\circ$ , and the anhydrous salt at  $260^\circ$ . The crystals are soluble in water. H. Vohl, and A. Bette prepared **ammonium zinc ferrous sulphate**,  $2(\text{NH}_4)_2\text{SO}_4 \cdot \text{ZnSO}_4 \cdot \text{FeSO}_4 \cdot 12\text{H}_2\text{O}$ , and **potassium zinc ferrous sulphate**,  $2\text{K}_2\text{SO}_4 \cdot \text{ZnSO}_4 \cdot \text{FeSO}_4 \cdot 12\text{H}_2\text{O}$ , from a mixed soln. of the three constituent salts. They are probably isomorphous mixtures. D. Ostersetzer found that hexahydrated ammonium ferrous sulphate and hexahydrated ammonium zinc sulphate form solid soln. in all proportions, and that the effect of temp. is insignificant. Expressing the concentrations in grams per 100 c.c. of sat. soln., at  $7^\circ$ :

Soln. {Fe-salt	279·49	236·84	220·24	158·60	101·64	54·36	0
{Zn-salt	0	18·99	22·47	46·88	70·93	92·10	125·50
Sp. gr. soln.	1·1541	1·1454	1·1392	1·1203	1·1051	1·0912	1·0794
Fe-salt in solid	100	85·7	76·57	49·52	29·51	13·18	0 mol. %

B. Haber-Chuwis observed similar phenomena with the hexahydrated potassium ferrous sulphate and hexahydrated potassium zinc sulphate, at  $6\cdot8^\circ$ :

Soln. {Fe-salt	329·15	275·03	203·22	142·76	119·46	68·10	0
{Zn-salt	0	19·39	47·62	63·87	67·83	77·78	113·62
Sp. gr. soln.	1·2067	1·1859	1·1600	1·1339	1·1204	1·0993	1·0795
Fe-salt in solid	100·00	93·55	81·98	69·45	64·29	47·22	0 mol. %

According to A. Étard, **zinc ferrous hydrosulphate**,  $2\text{ZnSO}_4 \cdot 2\text{FeSO}_4 \cdot \text{H}_2\text{SO}_4$ , is formed in rose-coloured crystals by adding a large excess of conc. sulphuric acid to a conc. soln. of the component salts and heating to about  $200^\circ$ . A. F. Walter von Escher observed that in the electrolysis of neutral and feebly acidic soln. of equimolar proportions of zinc and ferrous sulphates, at ordinary temp., zinc is precipitated almost free from iron; and that variations in the current density have very little influence on the composition of the cathode deposit. If the ferrous salt predominates, raising the temp., and decreasing the current density reduces the deposition potential of the iron, so that more iron is deposited. The iron can act as a depolarizer on the zinc deposit. At high temp. and with soln. rich in iron, the proportion of zinc deposited with the iron attains a maximum with increasing current densities. The zinc then acts as a depolarizer in the separation of iron, and the cathode potential jumps to a value corresponding with the amount of zinc deposited, and the zinc is deposited at the cathode transition point. This polarizing effect of zinc goes so far that even with a concentration ratio  $\text{Fe} : \text{Zn} = 9 : 1$ , and a high current density, zinc is the chief constituent of the cathode deposit as soon as the transition point is passed. The polarizing effect of the zinc in the cathode deposit on the separation of iron is aided by the charging of the cathode with hydrogen. The composition of the cathode deposit is independent of the thickness of the layer. The polarization phenomena are explained by the assumption that hypothetical intermediate products are formed during the electrolytic separation of

these metals, and that in the case of the iron group of metals these intermediate products are slowly transformed. The transformation is retarded by zinc or hydrogen. E. C. Eckel described a mineral from Colorado,  $2(\text{FeSO}_4 \cdot 7\text{H}_2\text{O}) \cdot (\text{Cu}, \text{Zn})\text{SO}_4 \cdot 7\text{H}_2\text{O}$ .

J. W. Retgers did not obtain **cadmium ferrous sulphate**, but rather colourless, monoclinic crystals of the trihydrate or the tritrichohydrates,  $(\text{Cd}, \text{Fe})\text{SO}_4 \cdot 2\frac{2}{3}\text{H}_2\text{O}$ , with 0 to 0.26 per cent. of the hydrated ferrous salt, and 100 to 99.74 per cent. of the hydrated cadmium salt; and also pale green, monoclinic crystals of the heptahydrates with 51.08 to 100 per cent. of the ferrous salt, and 48.92 to 0 per cent. of the cadmium salt. W. Stortenbeker examined the composition of soln. and crystals and found that with 100 to 79.8 molar per cent. of cadmium in soln., the crystals of  $(\text{Cd}, \text{Fe})\text{SO}_4 \cdot 2\frac{2}{3}\text{H}_2\text{O}$  contained 100 to 99.1 molar per cent. of cadmium, and with 79.8 to 0 molar per cent. of cadmium in soln., the crystals of  $(\text{Cd}, \text{Fe})\text{SO}_4 \cdot 7\text{H}_2\text{O}$  contained 36.6 to 0 molar per cent. of cadmium. The results are plotted in Fig. 659.

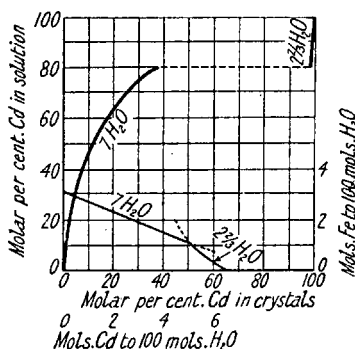


FIG. 659.—Relation between the Composition of Soln. and of Crystals of Cadmium and Ferrous Sulphates.

Yellowish or greenish-white, silky fibres or needles of a **ferrous aluminium sulphate**,  $\text{FeSO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ , occur at Bodenmais, and Mörsfeld, in Bavaria; Uramia, in Persia; Hurlet and Campsie, near Glasgow; Björkbackagård, in Finland; Tierra Amarilla, Chile; Iceland; Rossville, New York; Silver City, New Mexico; Tepeji, Mexico; East Greta, New South Wales, etc. Reports of analyses of the salt were made by M. H. Klaproth, J. D. Dana, A. E. Arppe, C. F. Rammelsberg, G. Forchhammer, A. Scacchi, G. Linck, E. H. S. Bailey, E. Dietrich, A. Brunner, S. Singer, V. R. von Zepharovich, F. W. Clarke, J. C. H. Mingaye, T. P. Lippitt, P. Berthier, R. Phillips, R. Brandes, etc. It was called *hversalt* by G. Forchhammer; *halotrichine* by A. Scacchi; and **halotrichite**—from *ἄλς*, salt, and *θρίξ*, hair—by E. F. Glocker. The term halotrichite was wrongly applied by J. F. L. Hausmann to alunogen. It is also called *hair-salt*, and *feather alum*. The term *mountain butter*, or *Berg-butter*, is applied to an impure efflorescence of a buttery consistency oozing from some alum slates. The crystals are monoclinic or triclinic. The crystals were examined by G. Linck, J. Uhlig, G. Cesaro, and A. Arzruni. D. Paterson found the salt as an efflorescence on bricks which had been exposed continuously to sulphur dioxide in bleaching chambers. When broken up, the mass exhibited a silky or fibrous texture like asbestos. F. Wirth, and C. Klauer prepared the salt by concentrating a soln. of equimolar proportions of the component salts. Ordinary ferrous sulphate crystallizes out first, and after that, ferrous aluminium sulphate. The crystals are washed with alcohol and ether. The salt appears white, and has a green fluorescence; it is readily soluble in water; 18 of the 24 mols. of water are expelled at  $100^\circ$ , and the remainder above this temp. The salt melts on warming, and decomposes forming oxides at a high temp. A. Étard prepared white, hexagonal plates of **ferrous aluminium hydrosulphate**,  $2\text{FeSO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4$ , by adding an excess of conc. sulphuric acid to a cold, conc. soln. of the component salts, and heating it to  $200^\circ$ . The ternary system, at  $25^\circ$ , was studied by V. J. Occleshaw, Fig. 660. The two salts mutually depress each other's solubility. There are three solubility curves. Hydrated aluminium sulphate,  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ , is the stable solid phase in contact with soln. containing less than 4.13 per cent. ferrous sulphate,  $\text{FeSO}_4$ . At this point the soln. contains 25.4 per cent. aluminium sulphate,  $\text{Al}_2(\text{SO}_4)_3$ . From this point, until a liquid phase is reached containing 10.17 per cent.  $\text{FeSO}_4$  and 20.16 per cent.  $\text{Al}_2(\text{SO}_4)_3$ , the stable solid in contact with the soln. is a double salt of the composition,  $\text{FeSO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ , corresponding to the alums.

With higher concentrations of ferrous sulphate the soln. are in contact with ferrous sulphate heptahydrate,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , as the stable solid. There is a congruent point on the curve corresponding to the double salt. This was confirmed experimentally by crystallizing the double salt from a soln. containing ferrous sulphate

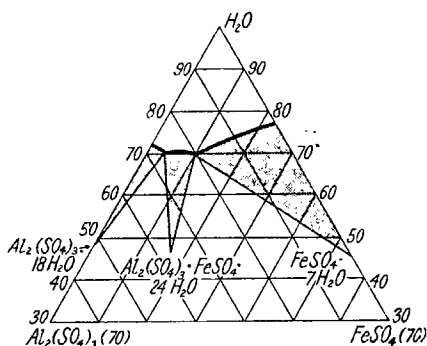


FIG. 660.—The Ternary System :  
 $\text{Al}_2(\text{SO}_4)_3\text{--FeSO}_4\text{--H}_2\text{O}$ , at  $25^\circ$ .

A. Etard obtained **ferrous chromic hydrosulphate**,  $2\text{FeSO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ , by the method employed for the corresponding aluminium salt.

G. Werther, and J. E. Willm prepared **thallous ferrous sulphate**,  $\text{TL}_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ , from a soln. of the component salts. The salt was also prepared by A. Benrath. The pale green, monoclinic prisms were found by G. Werther to have the axial ratios  $a : b : c = 0.7366 : 1 : 0.4964$ , and  $\beta = 105^\circ 52'$ . A. E. H. Tutton also found that the pale green crystals are monoclinic, with the axial angles  $a : b : c = 0.7427 : 1 : 0.4999$ , and  $\beta = 106^\circ 16'$ . The topic axial ratios are,  $\chi : \psi : \omega = 6.2050 : 8.3547 : 4.1765$ . The usual cleavage is parallel to (201). The sp. gr. is 3.650, and the mol. vol. 207.84. The optic axial angles are for the

	Li-	C-	Na-	Tl-	Cd-	F-lines
$2E'$	$129^\circ 35'$	$129^\circ 45'$	$131^\circ 35'$	$133^\circ 47'$	$135^\circ 26'$	$137^\circ 20'$
$2V_a$	$68^\circ 44'$	$68^\circ 46'$	$69^\circ 0'$	$69^\circ 26'$	$69^\circ 43'$	$69^\circ 59'$

The refractive indices are for the

	Li-	C-	Na-	Tl-	Cd-	F-	G-lines
$\alpha$	1.5880	1.5886	1.5929	1.5980	1.6009	1.6040	1.6115
$\beta$	1.6041	1.6048	1.6093	1.6146	1.6175	1.6209	1.6285
$\gamma$	1.6110	1.6117	1.6162	1.6223	1.6256	1.6292	1.6370

and the general formula for the  $\beta$ -index is  $1.5916 + 4.20091\lambda^{-2} + 71302000000000\lambda^{-4} +$  and if the constant 1.5916 be reduced by 0.0164, the formula represents the  $\alpha$ -index, and the  $\gamma$ -index if it be reduced by 0.0069. The sp. refractions with  $\mu^2$ -formula are, for the C-ray,  $\alpha = 0.0923$ ,  $\beta = 0.0943$ , and  $\gamma = 0.0952$ ; and for the  $H_\gamma$ -ray,  $\alpha = 0.0952$ ,  $\beta = 0.0973$ , and  $\gamma = 0.0983$ . The corresponding sp. dispersions,  $\mu_\sigma - \mu_c$ , are  $\alpha = 0.0029$ ,  $\beta = 0.030$ , and  $\gamma = 0.0031$ . The mol. refractions for the C-ray are  $\alpha = 70.00$ ,  $\beta = 71.56$ , and  $\gamma = 72.22$ ; and for the  $H_\gamma$ -ray,  $\alpha = 72.20$ ,  $\beta = 73.81$ , and  $\gamma = 74.60$ ; so that the mol. dispersions are  $\alpha = 2.2$ ,  $\beta = 2.25$ , and  $\gamma = 2.38$ . The mol. refractions with the  $\mu$ -formula and the C-ray are  $\alpha = 122.23$ ,  $\beta = 125.70$ , and  $\gamma = 127.14$ —mean 125.05. G. Werther found that the crystals do not effloresce, but the surfaces become dull. The salt loses all its water at  $120^\circ$ , and at a red-heat forms oxides with the loss of sulphur trioxide. The salt sinters slowly without melting when it is heated.

A. Scott prepared **manganous ferrous sulphate**,  $\text{MnSO}_4 \cdot \text{FeSO}_4 \cdot 2\text{H}_2\text{O}$ , in faint pink crystals, from a conc. soln. of the component salts treated with sulphuric acid in large excess. The salt may be an isomorphous mixture, because A. McL. White observed that the mutual, percentage solubility of ferrous and manganous sulphate, is :

	0°				25°				
MnSO <sub>4</sub>	3.07	10.66	19.18	31.84	39.39	37.83	36.95	13.57	0.09
FeSO <sub>4</sub>	12.55	9.26	5.69	0.14	0.33	1.33	1.82	14.39	23.09
Solid phase	Heptahydrate solid solution				Pentahydrate solid soln.	Transition point	Heptahydrate solid solution		

Observations were also made by J. W. Retgers. H. Vohl obtained **ammonium manganous ferrous sulphate**,  $2(\text{NH}_4)_2\text{SO}_4 \cdot \text{MnSO}_4 \cdot \text{FeSO}_4 \cdot 12\text{H}_2\text{O}$ , and also **potassium manganous ferrous sulphate**,  $3\text{K}_2\text{SO}_4 \cdot \text{MnSO}_4 \cdot \text{FeSO}_4 \cdot 12\text{H}_2\text{O}$ , from soln. of the three component salts. These triple salts may be isomorphous mixtures.

P. C. Ray and P. B. Sarkar<sup>4</sup> prepared monoclinic crystals of a series of isomorphous salts with one member **ammonium ferrous sulphatofluoberyllate**,  $(\text{NH}_4)_2\text{BeF}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ , where Ni, Co, Mn, Cd, Zn, and Mg may take the place of Fe. The salt was discussed by H. Seifert.

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### § 45. Ferric Sulphate

Anhydrous ferric sulphate,  $\text{Fe}_2(\text{SO}_4)_3$ , was analyzed by T. Thomson.<sup>1</sup> The salt unites with water to form a number of hydrates, some of which have been reported

as chemical individuals, but this does not give them all a *locus standi* in the list of chemical compounds. The hydrated forms are :

Dodecahydrate, $\text{Fe}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$	. . . . .	Ihleite.
Decahydrate, $\text{Fe}_2(\text{SO}_4)_3 \cdot 10\text{H}_2\text{O}$	. . . . .	Quenstedite.
Enneahydrate, $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$	{ hexagonal . . . . .	Coquimbite.
	{ rhombic . . . . .	Janosite.
Hemipentadecahydrate, $\text{Fe}_2(\text{SO}_4)_3 \cdot 7\frac{1}{2}\text{H}_2\text{O}$	. . . . .	Kornelite.
Heptahydrate, $\text{Fe}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$	. . . . .	
Hexahydrate, $\text{Fe}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$	. . . . .	Lausenite.
Tetrahydrate, $\text{Fe}_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$	. . . . .	
Trihydrate, $\text{Fe}_2(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$	. . . . .	
Dihydrate, $\text{Fe}_2(\text{SO}_4)_3 \cdot 2\text{H}_2\text{O}$	. . . . .	

**The preparation of ferric sulphate.**—Anhydrous ferric sulphate was found by G. Keppeler to be formed by the action of sulphur trioxide or sulphur dioxide and oxygen on ferric oxide :  $2\text{Fe}_2\text{O}_3 + 6\text{SO}_2 + 3\text{O}_2 \rightleftharpoons 2\text{Fe}_2(\text{SO}_4)_3$ , or  $\text{Fe}_2\text{O}_3 + 3\text{SO}_3 \rightleftharpoons \text{Fe}_2(\text{SO}_4)_3$ . The reaction is not perceptible at  $200^\circ$ , it begins about  $230^\circ$ , and is very marked at  $450^\circ$ ; it is retarded if moisture be present. The reaction was studied by G. Keppeler and J. d'Ans, G. Lunge and L. Pollit, F. Wöhler and co-workers, and B. Neumann and E. Goebel—*vide* sulphur trioxide, 10. 57, 337. As indicated in connection with ferrous sulphate, some ferric sulphate is formed during the weathering of iron pyrites. C. Dittler, for instance, observed that it is formed when oxygen acts on a slurry of ground marcasite. G. Keppeler reported the sulphate to be formed as an intermediate stage in the action of sodium chloride on pyrite at an elevated temp. :  $2\text{FeS}_2 + 2\text{NaCl} + 8\text{O}_2 = \text{Fe}_2(\text{SO}_4)_3 + \text{Na}_2\text{SO}_4 + \text{Cl}_2$ ; R. Saxon also observed ferric sulphate to be formed during the electrolysis of sulphuric acid using iron pyrite as cathode. J. d'Ans, and B. Neumann represented the action of heat on ferrous sulphate whilst air is excluded,  $6\text{FeSO}_4 \rightleftharpoons \text{Fe}_2(\text{SO}_4)_3 + 2\text{Fe}_2\text{O}_3 + 3\text{SO}_2$ ; F. Warlimont represented the action of oxygen :  $6\text{FeSO}_4 + 3\text{O} \rightleftharpoons 2\text{Fe}_2(\text{SO}_4)_3 + \text{Fe}_2\text{O}_3$ ; and G. Keppeler and J. d'Ans, the action of sulphur trioxide :  $2\text{FeSO}_4 + 2\text{SO}_3 = \text{SO}_2 + \text{Fe}_2(\text{SO}_4)_3$ —this reaction occurs only at a low temp., because at a high temp. the product is dependent on the composition of the gas-phase. A. Recoura observed that if hydrated ferric sulphate be heated to  $175^\circ$  it produces a yellow modification of the anhydrous salt; and similarly also when the acid ferric sulphates are heated. R. Scharizer observed that monohydrated ferric sulphate is formed at  $128^\circ$ , and the anhydrous salt at  $135^\circ$ ; F. Wirth and B. Bakke recommended  $175^\circ$  for the anhydrous salt; and H. Saito found that the enneahydrate is completely dehydrated in air at  $250^\circ$ —Fig. 669—and at  $230^\circ$  in air with 5 per cent. of sulphur dioxide. M. Lachaud and C. Lepière also prepared the anhydrous salt by the thermal decomposition of ammonium ferric sulphate, or by heating ferrous ammonium sulphate repeatedly in the presence of ammonium sulphate.

According to A. Vesterberg, J. Loczka, P. Hart, F. Ulrich, V. von Lang, and A. W. Davidson, if hydrated ferric sulphate be treated with conc. sulphuric acid, anhydrous ferric sulphate is formed as the solid phase; and E. Posnjak and H. E. Merwin observed that the anhydrous salt appears as the solid phase at  $140^\circ$  when the percentage proportions of  $\text{Fe}_2\text{O}_3$  :  $\text{SO}_3$  :  $\text{H}_2\text{O}$ , are 0.08 to 0.64 : 74.95 to 53.51 : 24.97 to 46.05; and at  $200^\circ$ , when these proportions are 0.04 to 1.5; 76.17 to 50.5 : 23.79 to 48.0—cf. Figs. 661 to 668.

**The preparation of the hydrates of ferric sulphate.**—A. Vesterberg prepared a soln. of ferric sulphate by dissolving *ferrum reductum* in hot sulphuric acid (1 : 1), evaporating the soln., and keeping it boiling for a couple of days until a reddish crystalline powder of anhydrous ferric sulphate is formed. Anhydrous ferric sulphate was also prepared by P. Hart, G. Fownes, W. B. Giles, E. Divers and T. Shimidzu by dissolving powdered heptahydrated ferrous sulphate in boiling conc. sulphuric acid :  $2\text{FeSO}_4 + \text{H}_2\text{SO}_4 = \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2$ . J. Milbauer and O. Quadrant recommended boiling 10 grms. of heptahydrated ferrous sulphate with 100 c.c.

of conc. sulphuric acid for about an hour; the bulk of the acid is then to be poured away, and the residue washed with alcohol, and finally with dry ether. The salt is then to be dried to constant weight. J. Loczka said that ferrous sulphide, marcasite, or pyrite can be similarly treated with conc. sulphuric acid. G. T. Gerlach, and S. U. Pickering commented on the difficulty in removing the excess of sulphuric acid from the product, and recommended heating the product until it assumes a light brown colour when hot, and has a pink colour when cold—the coloration is attributed to the presence of some ferric oxide. To remove the excess of acid from the ferric sulphate, C. R. C. Tichborne recommended heating the product for some days at 75°; A. Recoura recommended 120° to 150°; and G. Keppeler and J. d'Ans, M. Bodenstein and T. Suzuki, and E. Kothny, 400° to 450°.

L. J. Thénard, K. Seubert and R. Rohrer, F. K. Cameron and W. O. Robinson, and C. P. Prückner obtained a soln. of ferric sulphate by dissolving ferric oxide, or hydrated ferric oxide, or basic ferric sulphate in sulphuric acid. R. C. Wells obtained a soln. of ferric sulphate with the ratios  $\text{Fe}_2\text{O}_3 : \text{SO}_3 = 1 : 3$ , by dissolving freshly-precipitated hydrated ferric oxide in a soln. of ordinary ferric sulphate, and then adding the calculated quantity of sulphuric acid. When an aq. soln. of ferrous sulphate is exposed to air, or boiled with a suitable oxidizing agent, freed from the oxidizing agent by boiling or by repeated solution and evaporation to dryness, ferric sulphate is formed. This method was employed by C. F. Bucholz, C. R. C. Tichborne, M. Berthelot, and G. Keppeler and J. d'Ans. A. Recoura recommended removing the nitric acid by heating the dried product some days at 120°, and then at 140°. L. W. Pissarjewsky employed hydrogen dioxide as oxidizing agent in place of nitric acid.

F. Ulrich found crystals of ferric sulphate accidentally formed in a platinum dish used for concentrating sulphuric acid. A. and P. Buisine obtained ferric sulphate by the action of sulphuric acid of sp. gr. 1.53 to 1.82, on roasted pyrites. C. Dreyfus obtained ferric sulphate from waste sulphuric acid and waste iron residues; E. Hermite and A. Dubosc, by the electrolysis of a soln. of ferrous sulphate to which a dil. soln. of ferrous, sodium, potassium, calcium, vanadium, or magnesium chloride had been added.

As indicated below, the aq. soln. of ferric sulphate is readily hydrolyzed, and, as is so frequently the case with salts prone to hydrolysis, chemists in the past have recorded a list of basic salts, and nature too has here played her part, so that many of the basic salts have been recorded as special minerals. So far as chemical analyses can tell, there might be an indefinitely large number of products when there is no break in the continuity of the process of transformation, by hydrolysis, from pure ferric sulphate to pure ferric hydroxide. S. U. Pickering, and F. K. Cameron and W. O. Robinson would make a drastic sweep of the numerous basic salts which have been obtained artificially or reported as minerals, from the list of chemical individuals, by denying their existence as chemical compounds. F. K. Cameron and W. O. Robinson regard them all as either mixtures or solid soln. whose composition depends on arbitrary conditions of concentration, temperature, or pressure. S. U. Pickering maintained that only one basic salt exists as a chemical individual, namely  $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{Fe}_2\text{O}_3$ . Many of the synthesized products, formed by precipitation, hydrolysis, or fractional evaporation, were obtained under conditions where equilibrium could not have been attained, so that mixtures were produced. The slowness at which the products react with water gave the impression that definite, stable compounds were formed. The stability was only apparent, not real. F. K. Cameron and W. O. Robinson were guided in their work by the phase rule, and from their study of the system  $\text{Fe}_2\text{O}_3\text{--SO}_3\text{--H}_2\text{O}$ , at 25°, they inferred: (i) no definite basic sulphates are formed at this temp., but a stable solid phase with up to about 25 per cent. of  $\text{H}_2\text{SO}_4$  is one of a series of solid soln. involving these three constituents; (ii) decahydrated normal ferric sulphate is the stable solid phase with soln. containing 25 to 28 per cent. of sulphuric acid; and (iii) the stable solid phase with soln. containing 28 per cent. of sulphuric acid has the

composition:  $\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 10\text{H}_2\text{O}$ . These conclusions have not been confirmed by subsequent workers.

F. Wirth and B. Bakke studied the system  $\text{Fe}_2\text{O}_3\text{--SO}_3\text{--H}_2\text{O}$  at  $25^\circ$ . They were unable to establish the existence of definite solid phases in equilibrium with soln. containing less than 26 per cent. of  $\text{SO}_3$ , but they confirmed the existence of the basic salt  $2\text{FeO}_3 \cdot 5\text{SO}_3 \cdot 17\text{H}_2\text{O}$  occurring in two forms corresponding with the mineral  $\alpha$ - and  $\beta$ -copiapite; they also found crystals of ennea-hydrated ferric sulphate, and of the acid salt  $\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$ . M. P. Applebey and S. H. Wilkes obtained the results, summarized in Figs. 661 and 662, at  $25^\circ$ , when the concentrations are expressed in grams per 100 grms. of sat. soln.:

$\text{Fe}_2\text{O}_3$	0.27	3.88	8.04	13.80	17.52	18.56	19.98	7.91
$\text{SO}_3$	39.77	33.20	13.80	30.02	29.85	29.98	29.19	9.18
	$\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$		$\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 7\text{H}_2\text{O}$		$7\text{Fe}_2\text{O}_3 \cdot 15\text{SO}_3$		Solid solution	

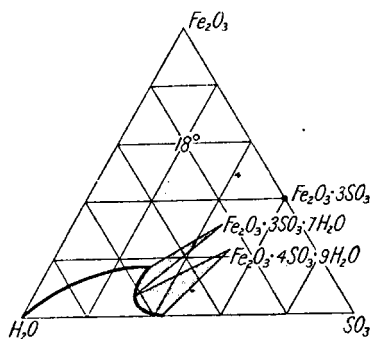


FIG. 661.—Equilibrium in the System:  $\text{Fe}_2\text{O}_3\text{--SO}_3\text{--H}_2\text{O}$ , at  $18^\circ$ .

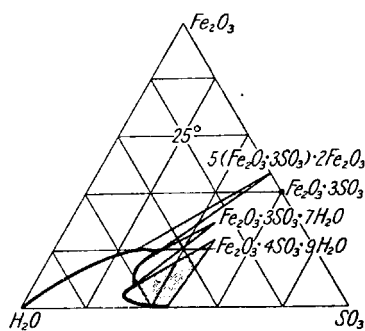


FIG. 662.—Equilibrium in the System:  $\text{Fe}_2\text{O}_3\text{--SO}_3\text{--H}_2\text{O}$ , at  $25^\circ$ .

The basic salt  $7\text{Fe}_2\text{O}_3 \cdot 15\text{SO}_3$  does not appear in the system at  $18^\circ$ . According to E. Posnjak and H. E. Merwin, in these experiments allowance was not always made for the fact, reported by A. Maus, that (i) soln. of ferric sulphate dissolve precipitated ferric oxide; (ii) ferric oxide adsorbs ferric sulphate from its soln.; and (iii) equilibria are obtained with great sluggishness in viscid soln. The following is a selection of the results of E. Posnjak and H. E. Merwin at  $200^\circ$  where concentrations are represented in grams per 100 grms. of sat. soln.:

$\text{Fe}_2\text{O}_3$	0.56	0.63	1.69	3.50	2.00	1.91	1.35	0.04
$\text{SO}_3$	4.90	5.58	11.39	19.43	41.87	48.94	52.12	76.17
	$\text{Fe}_2\text{O}_3$		$\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot \text{H}_2\text{O}$				$\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3$	

and they are plotted in Fig. 663. The results at  $140^\circ$  were:

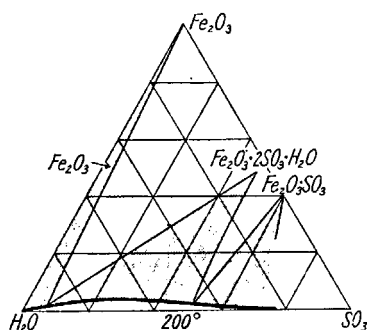


FIG. 663.—Equilibrium in the System:  $\text{Fe}_2\text{O}_3\text{--SO}_3\text{--H}_2\text{O}$ , at  $200^\circ$ .

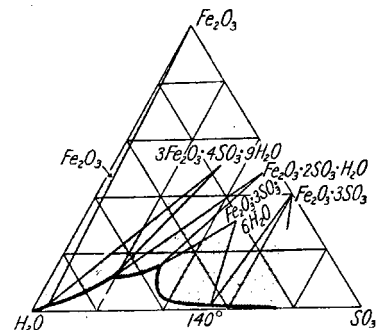


FIG. 664.—Equilibrium in the System:  $\text{Fe}_2\text{O}_3\text{--SO}_3\text{--H}_2\text{O}$ , at  $140^\circ$ .

$\text{Fe}_2\text{O}_3$	0.01	0.05	1.18	9.84	12.05	15.35	3.71	0.64	0.08
$\text{SO}_3$	0.82	2.60	4.06	17.65	22.39	30.88	37.10	53.31	74.95
	$\text{Fe}_2\text{O}_3$		$3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$		$\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot \text{H}_2\text{O}$		$\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 6\text{H}_2\text{O}$		$\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3$

and they are plotted in Fig. 664. The results at  $110^\circ$  are :

$\text{Fe}_2\text{O}_3$	0.01	0.08	14.51	19.74	19.04	1.26	0.81	0.48	0.15	0.06
$\text{SO}_3$	0.53	0.83	22.71	30.80	30.97	41.38	45.45	53.45	59.80	72.50
	$\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$		$3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$		$\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot \text{H}_2\text{O}$		$\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 6\text{H}_2\text{O}$		$\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 3\text{H}_2\text{O}$	

and they are plotted in Fig. 665. The results at  $75^\circ$  are :

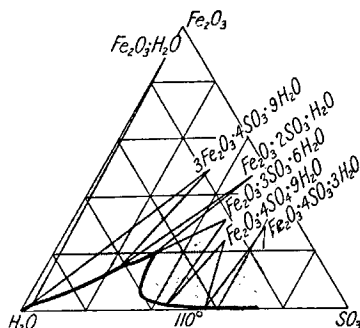


FIG. 665.—Equilibrium in the System :  $\text{Fe}_2\text{O}_3$ — $\text{SO}_3$ — $\text{H}_2\text{O}$ , at  $110^\circ$ .

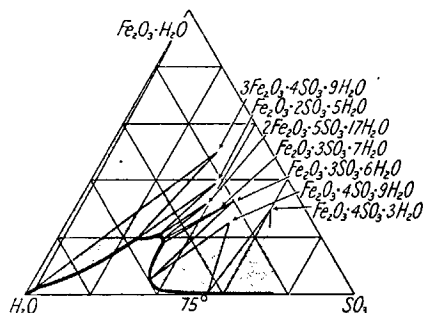


FIG. 666.—Equilibrium in the System :  $\text{Fe}_2\text{O}_3$ — $\text{SO}_3$ — $\text{H}_2\text{O}$ , at  $75^\circ$ .

$\text{Fe}_2\text{O}_3$	0.34	0.93	17.78	20.93	18.13	4.59	0.12	0.12	0.07
$\text{SO}_3$	1.00	1.62	23.10	30.11	32.32	35.51	54.63	56.25	74.14
	$\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$		$3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$		$\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot \text{H}_2\text{O}$		$\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 6\text{H}_2\text{O}$		$\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 3\text{H}_2\text{O}$

and they are plotted in Fig. 666. The results at  $50^\circ$ , plotted in Fig. 667, are :

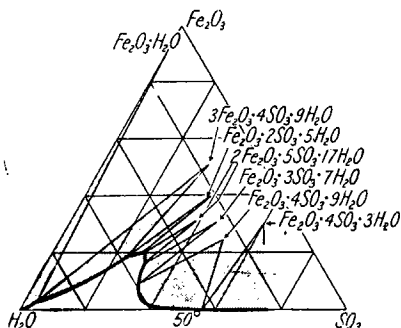


FIG. 667.—Equilibrium in the System :  $\text{Fe}_2\text{O}_3$ — $\text{SO}_3$ — $\text{H}_2\text{O}$ , at  $50^\circ$ .

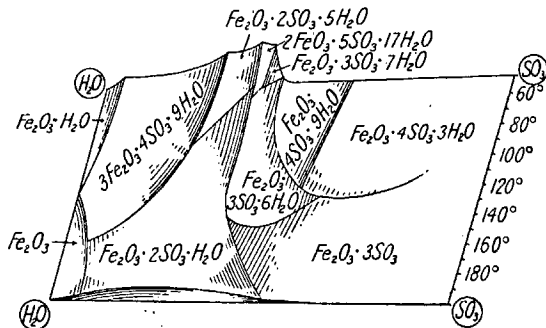


FIG. 668.—Equilibrium in the System :  $\text{Fe}_2\text{O}_3$ — $\text{SO}_3$ — $\text{H}_2\text{O}$ , from  $50^\circ$  to  $200^\circ$ .

$\text{Fe}_2\text{O}_3$	0.14	1.44	17.96	20.13	20.70	16.78	8.56	5.55	0.09	0.07	0.07
$\text{SO}_3$	0.39	2.30	22.96	27.18	28.40	30.72	32.56	33.96	55.34	59.20	75.37
	$\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$		$3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$		$\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot \text{H}_2\text{O}$		$\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 6\text{H}_2\text{O}$		$\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 3\text{H}_2\text{O}$		

All these results are represented as an equilibrium surface in Fig. 668. G. Tunell

and E. Posnjak studied the effect of copper sulphate on a portion of the system—*vide infra*.

A. Schrauf reported a *dodecahydrate*,  $\text{Fe}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$ , to occur in the graphite deposits of Mugrau, Bohemia; and he named it *ihleite*—after M. Ihle. Specimens were found elsewhere by R. von Görgy, and F. Slavik; and analyses were made by B. Erben, and A. Schrauf. R. Scharizer doubted the individuality of *ihleite*; he regarded it as a mixture of copiapite and rhomboclase; and E. Manasse considered it to be impure copiapite. No evidence of the dodecahydrate has been obtained in the equilibrium studied in the system  $\text{Fe}_2\text{O}_3\text{--SO}_3\text{--H}_2\text{O}$  at different temp.; and a similar remark applies to the *decahydrate*,  $\text{Fe}_2(\text{SO}_4)_3 \cdot 10\text{H}_2\text{O}$ , reported by G. A. Bertels, and A. C. Oudemans to separate from the soln. obtained by the action of nitric and sulphuric acids on ferrous sulphate. F. K. Cameron and W. O. Robinson said that the decahydrate is formed by the action of water or moisture on the anhydrous salt, and by shaking of a soln. of ferric sulphate with freshly-precipitated ferric hydroxide in soln. containing 25 to 28 per cent. of  $\text{SO}_3$  at  $25^\circ$ . E. Posnjak and H. E. Merwin do not consider the evidence satisfactory. G. Linck reported the mineral *quenstedtite*—named after F. A. Quenstedt—to be the decahydrate occurring with coquimbite and other sulphates at Tierra Amarilla, Copiapo, Chili.

In 1833, H. Rose reported the occurrence at Tierra Amarilla, Copiapo, Chili, of an *enneahydrate*,  $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ . This was confirmed by the analyses of G. Linck, H. F. Collins, J. B. Macintosh, C. Lausen, R. Scharizer, L. Darapsky, and R. Serrano. J. D. Dana, and C. Lausen gave  $2(\text{Fe}, \text{Al})_2\text{O}_3 \cdot 7\text{SO}_3 \cdot 22\text{H}_2\text{O}$ . J. D. Dana called the mineral *blakeite*—after W. P. Blake—but A. Breithaupt's earlier name *coquimbite* is generally employed, even though the mineral does not occur at Coquimbo, Chili. R. Scharizer said that the enneahydrate is obtained in hexagonal plates by evaporating to dryness a soln. of hydrated ferric oxide in an excess of sulphuric acid, and washing the product with alcohol. F. Wirth and B. Bakke observed that coquimbite is stable at ordinary temp. in soln. containing 31.54 to 27.98 per cent. of  $\text{SO}_3$ , 9.39 to 16.07 per cent. of  $\text{Fe}_2\text{O}_3$ , and 59.07 to 55.93 per cent. of water; M. P. Applebey and S. H. Wilkes, in soln. with 31.88 to 29.72 per cent.  $\text{SO}_3$ , 9.63 to 17.48 per cent. of  $\text{Fe}_2\text{O}_3$ , and 58.49 to 52.79 per cent. of  $\text{H}_2\text{O}$ ; and R. Scharizer said that this hydrate is the stable phase when the mol. quotient  $\text{SO}_3 : \text{Fe}_2\text{O}_3$  is greater than 3 and less than 4. H. Böckh described a rhombic form of the enneahydrate—coquimbite is hexagonal. The rhombic enneahydrate was called *janosite*, and it was obtained from Vashegy, Hungary. E. Weinschenk, E. Wülfing, W. H. Melville and W. Lindgren, Z. Toborffy, and R. Scharizer considered janosite to be impure copiapite. The sulphate from Leona Heights, California, described by W. T. Schaller, is probably a related mineral. According to A. Recoura, when a conc. soln. of ferrous sulphate is exposed to air for several days, it deposits a spongy, nodular, saffron-yellow mass consisting of the basic sulphate,  $6\text{Fe}_2(\text{SO}_4)_3 \cdot \text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ , impregnated with an acid sulphate of variable constitution which can be removed by extraction with absolute alcohol. When a specimen of the yellow mass having the composition  $\text{Fe}_2(\text{SO}_4)_3 \cdot 11\text{H}_2\text{O}$ , was treated with alcohol, 89 per cent. of the iron remained in the form of the basic sulphate. If the yellow mass is allowed to dry in air until it has reached the composition  $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ , the basic and acid sulphates recombine, and can no longer be separated by alcohol. The solidification of ferric sulphate on evaporation of its soln. takes place therefore in two stages. In consequence of this, the yellow mass is not homogeneous, but contains in some parts an excess of the basic, in others of the acid salt. If this is made into a paste with a little water and spread on a plate, at the end of 24 hrs. the ferric sulphate,  $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ , is obtained as a white, homogeneous layer. The ordinary form is yellow. A. Recoura added that the white and yellow hydrated ferric sulphates must differ in constitution. The yellow sulphate dissolves immediately in water, but the white modification does so only slowly. Whilst both sulphates are soluble in absolute alcohol without decomposition, the yellow modifi-

cation is decomposed to the insoluble basic sulphate and the soluble acid sulphate,  $\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3$ , on treatment with 95 per cent. alcohol, or with a little water, or on exposure to moist air, under which conditions the white modification is stable.

J. A. Krenner reported a rose-red or violet *hemipentadecahydrate*,  $\text{Fe}_2(\text{SO}_4)_3 \cdot 7\frac{1}{2}\text{H}_2\text{O}$ , to occur at Szomobnok, Hungary, and he called it **kornelite**—after Kornel Hlavacek. It was analyzed by J. Loczka; and it is considered to have been the heptahydrate. According to F. Wirth and B. Bakke, the enneahydrate is the normal salt stable at  $25^\circ$ , but M. P. Applebey and S. H. Wilkes found that in presence of sulphuric acid, the normal salt at  $18^\circ$  to  $25^\circ$  is the *heptahydrate*,  $\text{Fe}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$ . E. Posnjak and H. E. Merwin observed that the heptahydrate is stable in contact with its sat. soln. of sulphuric acid below  $80^\circ$ . Taking percentage proportions of the three constituents  $\text{Fe}_2\text{O}_3 : \text{SO}_3 : \text{H}_2\text{O}$ , E. Posnjak and H. E. Merwin showed that the stable phase, Figs. 666 and 667, is the heptahydrate, at  $75^\circ$ , when  $\text{Fe}_2\text{O}_3 : \text{SO}_3 : \text{H}_2\text{O}$  is 18.13 to 19.0 : 32.32 : 49.55 to 48.8, and at  $50^\circ$ , 7.5 to 16.78 : 33.0 to 30.72 : 59.5 to 52.5. M. P. Applebey and S. H. Wilkes, at  $25^\circ$ , gave 8.04 to 13.80 : 32.06 to 30.02 : 59.90 to 56.18, and at  $18^\circ$ , 9.63 to 18.68 : 31.88 to 29.64 : 58.49 to 51.68. E. Posnjak and H. E. Merwin said that whilst the heptahydrate is the stable phase between  $25^\circ$  and  $50^\circ$  under the conditions first indicated, the stable phase between  $50^\circ$  and  $150^\circ$  is the *hexahydrate*,  $\text{Fe}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$ . Taking percentage proportions of  $\text{Fe}_2\text{O}_3 : \text{SO}_3 : \text{H}_2\text{O}$ , the hexahydrate appears at  $140^\circ$  when 0.64 to 15.5 : 53.31 to 31.5 : 46.05 to 53.0, at  $110^\circ$  when 1.0 to 20.0 : 43.0 to 31.0 : 56.0 to 49.0, and at  $75^\circ$  when 4.59 to 18.13 : 35.51 to 32.32 : 59.90 to 49.55. C. Lausen reported the hexahydrate to occur in monoclinic fibres in a mine in Arizona, and added that it was formed through the burning of some pyritic ores. It was named *rogersite*—after A. F. Rogers—but G. M. Butler said that since the name rogersite is used for another mineral, it would be more appropriate to call it **lausenite**—after C. Lausen.

According to A. Recoura, if the white enneahydrate be kept for some time at a temp. a little below  $100^\circ$ , it furnishes the *trihydrate*,  $\text{Fe}_2(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$ , and at  $175^\circ$  it forms a brownish-yellow anhydrous salt, which dissolves in water very much more rapidly than that obtained by dehydrating the yellow enneahydrate. The brownish-yellow, anhydrous salt furnishes the trihydrate when exposed to moist air. R. Scharizer found that the enneahydrate coquimbite loses no water when confined over conc. sulphuric acid, but at  $83^\circ$  water begins to be evolved so that at  $93^\circ$ , 5 mols. are given off, and a *tetrahya*te,  $\text{Fe}_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$ , remains; at  $113^\circ$  more water is evolved so that at about  $161^\circ$ , the *dihydrate*,  $\text{Fe}_2(\text{SO}_4)_3 \cdot 2\text{H}_2\text{O}$ , remains. Above  $161^\circ$  the hydrate slowly passes into the anhydrous salt. The dehydration curve, Fig. 669, shows three breaks respectively at  $83^\circ$ ,  $93^\circ$ , and  $161^\circ$ .

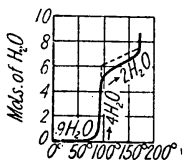


FIG. 669.—The Dehydration Curve of Coquimbite,  $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ .

**The physical properties of ferric sulphate.**—The colour of anhydrous ferric sulphate has been called white, grey, pale yellow, and rose. Actually, the colour depends on the degree of purity, the temp., and the grain-size. According to S. U. Pickering, the powder is pale brown when hot and rose-red when cold. The coloration here is no doubt due to the presence of ferric oxide, since G. Keppeler and J. d'Ans found that at ordinary temp., the salt is white by reflected light, and pale bluish-green by transmitted light; whilst E. Posnjak and H. E. Merwin said that the colour is yellowish-grey when the grain-size exceeds 0.1 mm. According to A. Laurent, and A. Recoura, there are two **allotropic forms** of the anhydrous salt, one hexagonal and one rhombic. The former is white, the latter is yellow; and the former dissolves in water more slowly than the latter. F. Wirth and B. Bakke, however, showed that the alleged differences are simply effects of differences in the grain-size of the alleged forms, but his products may have been the same but in different states of subdivision. E. Posnjak and H. E. Merwin found that in their study of the ternary system, the anhydrous ferric sulphate usually appeared

in two different crystalline forms, both together. The **crystals** of both forms retained their optical properties when heated dry up to the temp. at which sulphur trioxide began to be evolved, so that their relative stability relations are unknown. Both forms hydrate slowly on exposure to air. The one form appears as flattened rhombs, greyish-yellow in colour, with the narrow prism faces over all the lateral edges, and having rhombohedral cleavage. The axial ratio of the rhombohedral crystals is  $a : c = 1 : 1.35$ , and the indices of refraction are  $\omega = 1.770$  and  $\epsilon = 1.760$ . The other form has a similar colour, and appears in thick tabular crystals flattened parallel to the base. The crystals belong to the rhombic system, and have the axial ratios  $a : b : c = 0.957 : 1 : 1.357$ ; R. Scharizer gave  $0.9857 : 1 : 1.3991$ ; and V. von Lang reported some crystals with the vertical axis about half this length, for he gave  $a : b : c = 1.0855 : 1 : 0.6715$ . E. Posnjak and H. E. Merwin found the optic axial angle  $2V = 60^\circ$  nearly. G. M. Smith represented the white salt, which dissolves slowly, by the formula  $\text{Fe}[\text{Fe}(\text{SO}_4)_3]$  or  $\text{Fe}[\text{Fe}(\text{SO}_4)_2]_3$ .

G. Linck reported that quenstedtite, the decahydrate, occurs in reddish-violet, tabular crystals parallel to (010), in elongated crystals parallel to (100) like gypsum, and in crystals with the clino dome faces striated parallel to (100). The monoclinic crystals have the axial ratios  $a : b : c = 0.39397 : 1 : 0.40584$ , and  $\beta = 78^\circ 7\frac{1}{2}'$ . The (010)-cleavage is perfect; and the (100)-cleavage is less well-defined and it yields a fibrous fracture. The optical character is negative. Coquimbite, the enneahydrate, sometimes occurs in colourless, white, yellowish-, greenish-, or brownish-white, or lavender-tinted crystals which sometimes have a tinge of violet or amethyst-blue; it may also occur granular and massive; or more commonly in hexagonal prisms, or in rhombohedral forms which sometimes simulate octahedra. H. Ungemach observed that the triclinic mineral has the axial ratios  $a : b : c = 0.2621 : 1 : 0.2776$ , and  $\alpha = 94^\circ 10'$ ,  $\beta = 101^\circ 44.5'$ , and  $\gamma = 96^\circ 18.5'$ . G. Linck found that the rhombohedral crystals have the axial ratio  $a : c = 1 : 1.5613$ , and  $\alpha = 80^\circ 6'$ . Twinning may occur about the (0001)-plane; the (1120)-faces may coincide and show a reversed striation parallel to the edge (3032)/(1120). The prismatic cleavage is perfect, the (1010)-, (1011)-, and the (0111)-cleavages are imperfect. The optical character is positive. The corrosion figures are equilateral triangles corresponding with the rhombohedral symmetry. The voluminous, yellow mass which A. Recoura obtained by evaporating a conc. soln. of ferric sulphate was considered to be an allotropic form of the enneahydrate; the same modification was obtained by exposing the anhydrous sulphate to moist air. The yellow form is said to dissolve in much water more readily than the white salt. R. Scharizer inferred that the yellow form is really a mixture of a basic sulphate, copiapite, and an acid sulphate; F. Wirth and B. Bakke considered the yellow form to be copiapite mixed with some acid salt; and F. K. Cameron and W. O. Robinson supposed that the yellow and white forms are chemically the same, but in different degrees of purity, and state of subdivision. E. Posnjak and H. E. Merwin said that the coarse-grained powder of the heptahydrate is rose-pink, but larger crystals are colourless, monoclinic plates. The laths are elongated to (001), and flattened parallel to (010), and there are traces of polysynthetic twinning on (010), parallel to the elongation. The hexahydrate crystallizes readily, and it is stable in contact with salt. soln. from  $50^\circ$  to about  $150^\circ$ . The slender, colourless laths are elongated parallel to (001), and flattened parallel to (010). The crystals of the hexahydrate are monoclinic. H. Ungemach gave for coquimbite the hexagonal axial ratio  $a : c = 1 : 1.5643$ , and for the rhombohedral variety, **paracoquimbite**,  $a : c = 1 : 2.3464$ .

The **specific gravity** of anhydrous ferric sulphate was found by L. F. Nilson and O. Pettersson to be 3.097 at  $18.2^\circ$ ; M. Lachaud and C. Lepière gave 3.05 at  $14^\circ$ ; and G. Keppeler and J. d'Ans, 2.937. A. Schrauf gave 1.812 for the sp. gr. of the dodecahydrate, ihleite; and G. Linck, 2.116 for the sp. gr. of the decahydrate, quenstedtite at  $16.2^\circ$ . A. Breithaupt gave 2.092 for the sp. gr. of the enneahydrate, coquimbite, G. Linck, 2.105; C. Lausen, 2.092; and J. D. Dana, 2.0



to 2.1. B. Franz found the sp. gr. of aq. soln. of ferric sulphate at 17.5° to be :

$\text{Fe}_2(\text{SO}_4)_3$	5	10	15	20	30	40	50	60 per cent.
Sp. gr..	1.0426	1.0854	1.1324	1.1826	1.3090	1.4506	1.6148	1.8002

Results by G. T. Gerlach, and H. Hager were a little larger than the values found by B. Franz; thus, H. Hager gave for soln. with 10, 30, and 50 per cent. of  $\text{Fe}_2(\text{SO}_4)_3$ , the respective values 1.097, 1.337, and 1.650. B. Cabrera and E. Moles gave :

$\text{Fe}_2(\text{SO}_4)_3$	0.351	1.173	2.963	3.978	6.678	7.986	11.259	15.382 per cent.
Sp. gr.	1.0013	1.0080	1.0237	1.0340	1.0612	1.0730	1.1132	1.1525

Observations were also made by G. Lunge and E. Berl, W. Manchot and co-workers, S. U. Pickering, and A. Heydweiller. P. F. Gaehr represented the relation between the sp. gr.,  $D$ , and the percentage composition,  $C$ , by the relation:  $\log_{10} D = aC$ , where  $a$  is a constant. The **molecular volume** of the anhydrous salt, given by L. F. Nilson and O. Pettersson, is 129.16. G. Beck studied the subject. H. H. Stephenson discussed the contraction which occurs in the formation of the compound from its elements. G. T. Gerlach, and H. Hager calculated the change in vol. which occurs when ferric sulphate is dissolved in water. I. Traube discussed the mol. solution volume, and found that for soln. with 10, 30, and 50 per cent.  $\text{Fe}_2(\text{SO}_4)_3$ , the mol. soln. vol. are respectively 49.7, 68.4, and 84.9.

The **hardness** of quenstedtite is 2.5 on Mohs' scale, and that of coquimbite, 2.0 to 2.5. T. Redwood studied the **diffusion** of soln. of the salt through membranes; M. Torre found that for a soln. with 0.666 grm. of  $\text{Fe}_2(\text{SO}_4)_3$  per 100 c.c., at 30°, 40°, and 50°, the changes in concentration against water, in 24 hrs., were respectively 0.240, 0.256, and 0.268 grm. per 100 c.c.; and with a soln. with 0.133 grm.  $\text{Fe}_2(\text{SO}_4)_3$  per 100 c.c., respectively 0.044, 0.052, and 0.055. Z. H. Skraup discussed the **capillary rise** of soln. of ferric sulphate in filter-paper.

C. Montemartini and L. Losana found that the **thermal expansion** of a 30 per cent. soln. of ferric sulphate between 10° and 98°, on an arbitrary scale, exhibited a reversible break. L. F. Nilson and O. Pettersson found the **specific heat** of the anhydrous sulphate to be 0.1656 between 0° and 100°. F. M. Raoult observed the **lowering of the freezing-point** of a soln. of a gram of  $\text{Fe}_2(\text{SO}_4)_3$  in 100 c.c. of water to be 0.115°. A. Recoura made observations on the subject. R. Scharizer's observations on the **thermal decomposition** or dehydration of crystals of the enneahydrate are summarized in Fig. 669. F. Wirth and B. Bakke said that at 98°, the enneahydrate loses 5 mols. of water; in 8 hrs. at 125°, 8 mols.; and at 175° all the water is expelled; and A. Recoura found that 6 mols. are given off at 100°, and the remaining 3 mols. at 175°. J. d'Ans, and L. and P. Wöhler and W. Plüddemann said that at temp. exceeding 200°, in the absence of air, the reaction  $\text{Fe}_2(\text{SO}_4)_3 \rightleftharpoons \text{Fe}_2\text{O}_3 + 3\text{SO}_3$  occurs, and no basic sulphate or solid soln. of oxide in sulphate is formed. J. A. Hedvall and J. Heuberger found that in a current of nitrogen, the decomposition is perceptible at 660°. If a limited supply of air is available, H. O. Hofman and W. Wanjukoff found that the decomposition is complete at 530°; and K. Friedrich, and K. Friedrich and A. Blicke said 705°. K. Honda and T. Ishiwara found that ferric oxide begins to be formed at 660°. H. Saito observed that in a current of air, decomposition begins at 550°, and in a current of air with 5 per cent. of sulphur dioxide, at 620°. When the salt is heated in a closed vessel, under suitable conditions, a state of equilibrium is established. G. Keppeler found that the press. of the sulphur trioxide is imperceptible at 400°, but it is measurable at 500°. G. Keppeler and co-workers found that between 500° and 700°, the relation between the **dissociation pressure**,  $p$  mm., and the temp.,  $T^\circ \text{K}$ ., can be represented by  $\log p = 11.8626 - 44720/4.584T$ . In the gaseous phase there is another state of equilibrium:  $2\text{SO}_3 \rightleftharpoons 2\text{SO}_2 + \text{O}_2$ . They also found that the press. over the basic salt,  $\text{Fe}_2\text{O}(\text{SO}_4)_2$ , is less than is the case with the normal

sulphate at the same temp. L. and P. Wöhler and W. Plüddemann observed for the pressure  $p = p_{\text{SO}_3} + p_{\text{SO}_2} + p_{\text{O}_2}$  mm. :

	553°	592°	634°	660°	690°	699°	707°
$p$	23	45	113	182	401	560	715

and for the press. of the sulphur trioxide :

	580°	600°	620°	640°	660°	680°	700°
$p_{\text{SO}_3}$	24.7	36.6	50.5	70.6	93.5	133.5	233.0

Measurements were also reported by L. Wöhler and M. Grünzweig, G. Marchal, P. Grünzweig, F. Warlimont, W. Plüddemann, M. Bodenstein and T. Suzuki, and W. Reinders and F. Goudriaan. The results of L. and P. Wöhler and W. Plüddemann are summarized by the continuous curve, Fig. 670, and those of G. Keppeler and J. d'Ans, by the dotted curve, Fig. 670. Unlike G. Keppeler and J. d'Ans, L. and P. Wöhler and W. Plüddemann observed that with the basic sulphate,  $\text{Fe}_2\text{O}_3(\text{SO}_4)$ , the dissociation press. at three different temp. were the same as those obtained with the normal sulphate. This was taken to mean that basic sulphates are not formed in the thermal dissociation of ferric sulphate, and that there is no evidence of the formation of a solid soln. of oxide and sulphate. M. Bodenstein and T. Suzuki attributed the low results obtained by G. Keppeler and J. d'Ans to an insufficient allowance of time for equilibrium to be established; they also said that if ferric sulphate dissociates into ferric oxide and sulphur trioxide, an excess of trioxide instead of a deficit would be anticipated—a deficit was observed, meaning that the mechanism of the reaction is more complex than is represented by the equation:  $\text{Fe}_2(\text{SO}_4)_3 \rightleftharpoons \text{Fe}_2\text{O}_3 + 3\text{SO}_3$ . F. G. Jackson studied the thermal decomposition of ferric sulphate; and K. Flick, and H. H. Willard and R. D. Fowler, the separation of a mixture of sulphates by fractional thermal decomposition.

P. A. Favre and J. T. Silbermann made some observations on the **heat of formation** of ferric sulphate; J. A. Hedvall and J. Heuberger gave for the solid salt  $(2\text{Fe}_2\text{S}_3, 12\text{O}) = 640$  Cals.; J. Thomsen,  $(\text{Fe}_2\text{O}_3, 3\text{SO}_3) = 141.237$  Cals.; L. and P. Wöhler and W. Plüddemann gave 27.31 Cals. for the **heat of dissociation** of a mol of  $\text{SO}_3$  from a mol of  $\text{Fe}_2(\text{SO}_4)_3$  between 620° and 640°, but G. Keppeler and J. d'Ans obtained a smaller value. Calculations were also made by P. P. Budnikoff. For the heat of formation of the salt in soln., G. Keppeler and J. d'Ans gave  $(2\text{Fe}_2\text{S}_3, 12\text{O}, \text{Aq.}) = 659.5$  Cals.; M. Berthelot,  $(2\text{Fe}_2\text{O}_3, 3\text{SO}_3, \text{Aq.}) = 224.9$  Cals.; and J. Thomsen,  $(2\text{FeSO}_4\text{Aq.}, \text{O}, \text{SO}_3\text{Aq.}) = 38.5$  Cals. For the **heat of neutralization**, M. Berthelot gave  $(2\text{Fe}(\text{OH})_3, 3\text{H}_2\text{SO}_4\text{Aq.}) = 34.1$  Cals.; and J. Thomsen, 33.84 Cals. For the **heat of dilution** of a soln. of a mol of  $\text{Fe}_2(\text{SO}_4)_3$  in 0.67 litre of water with 1.33 litres, G. Lemoine gave 4.8 Cals.; and for a soln. of a mol of  $\text{Fe}_2(\text{SO}_4)_3$  in 2 litres of water with 2 and 6 litres of water, respectively 0.4 and 0.6 Cals. M. Berthelot gave for the dilution of a soln. of a mol of  $\text{Fe}_2(\text{SO}_4)_3$  in 2 litres, with 6 litres, 0.6 Cals.; and for the admixture of 12 litres of a soln. of a mol of  $\text{Fe}_2(\text{SO}_4)_3$  with 3 mols of  $\text{H}_2\text{SO}_4$  (a mol per 4 litres), 2.8 Cals. G. Beck made observations on the **free energy** of the salt.

E. Posnjak and H. E. Merwin measured the **index of refraction** of anhydrous ferric sulphate, and found for the hexagonal (trigonal) and rhombic forms :

		F-	Tl-	Na-	C-	Li-light	
Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	Trigonal	$\omega$	1.809	1.786	1.770	1.756	1.754
		$\epsilon$	1.798	1.775	1.760	1.746	1.744
		$\alpha$	1.844	1.819	1.802	1.787	1.785
	Rhombic	$\beta$	1.857	1.831	1.814	1.799	1.797
		$\gamma$	1.861	1.835	1.818	1.803	1.801

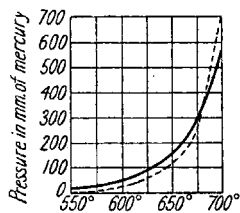


FIG. 670.—Dissociation Pressure of Ferric Sulphate.

G. Linck gave for the indices of refraction of the enneahydrate for red-light,  $\omega=1.5469$  and  $\epsilon=1.5508$ ; and for yellow-light,  $\omega=1.5519$  and  $\epsilon=1.5575$ ; A. Arzruni gave  $\omega=1.5376$  and  $\epsilon=1.5468$  for Li-light; and  $\omega=1.5455$  and  $\epsilon=1.5547$  for Na-light. C. Lausen gave for coquimbite,  $\epsilon=1.572$  and  $\omega=1.536$ . E. Posnjak and H. E. Merwin gave for the heptahydrate and the hexahydrate:

		F-	Tl-	Na-	C-	Li-light
$\text{Fe}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$	$\alpha$	1.585	1.578	1.572	1.566	1.565
	$\beta$	1.603	1.593	1.586	1.579	1.578
	$\gamma$	1.666	1.651	1.640	1.631	1.629
$\text{Fe}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$	$\alpha$	1.624	1.613	1.605	1.598	1.597
	$\beta$	1.656	1.644	1.635	1.627	1.626
	$\gamma$	1.668	1.667	1.657	1.648	1.645

C. Lausen gave for the monoclinic crystals of the hexahydrate, lausenite,  $\alpha=1.594$ ,  $\beta=1.628$ , and  $\gamma=1.654$ ; and the optical character is negative. E. Doumer made some observations on the refractive indices of aq. soln. L. R. Ingersoll's results for a soln. of ferric sulphate of sp. gr. 1.446, at  $23^\circ$ ; and C. E. Richards and R. W. Roberts's results for a soln. of sp. gr. 1.190, at  $17^\circ$ , are, for rays of wave-length  $\lambda$  A.:

	Sp. gr. 1.446				Sp. gr. 1.190			
$\lambda$	12,500	10,000	8000	6000	6104	5780	5330	4958
$\mu$	1.4061	1.4113	1.4160	1.4234	1.3728	1.3741	1.3768	1.3800

M. Kimura and M. Takewaki found that the **absorption spectrum** of anhydrous ferric sulphate shows an absorption band beginning at 4000 A. in the ultra-violet, and ending at 3400 A. E. Posnjak and H. E. Merwin added that both the trigonal and rhombic forms exhibit the same type of absorption. The colour of aq. soln. of ferric sulphate is dependent on the hydrolysis; by increasing the dilution or by raising the temp., the hydrolysis is favoured, and the colour changes from a yellowish- to a reddish-brown, and S. U. Pickering found that the intensity of the coloration with dilution increases to a maximum, and then remains constant, and as time goes on, the colour becomes darker and a turbidity appears. As pointed out by R. Weinland, the hydrolysis is reversed, and the colour of the soln. becomes paler when acid is added. J. S. Anderson found the mol. extinction coeff.,  $k$ , of soln. with 1.0 and 0.1 mol per litre, in layers 0.14 and 2 cm. thick, with light of wave-length  $\lambda$  A.:

$\lambda$	4340	4530	4990	5630	6020	6770	7460	9000	11,750
$k$ { 1.0	6.9	2.1	0.76	0.51	0.31	0.19	0.33	0.42	0.04
0.1	9.5	4.7	2.2	1.3	0.49	0.25	0.37	0.54	0.05

Observations were also made by T. Bayley, T. Ewan, G. Fuseya and K. Murata, R. A. Houstoun, R. A. Houstoun and C. Cochrane, R. A. Morton and R. W. Riding, and C. E. Richards and R. W. Roberts. M. Pierucci observed no spectral lines of iron when the dust of anhydrous ferric sulphate is sprayed in an arc-light.

M. Schneider found that a feebly acidified soln. of ferric sulphate is distinctly reduced by exposure to **light**, but not so much as is the case with a soln. of ferric chloride; and M. V. Dover observed that the degree of hydrolysis is perceptibly greater in light than it is in darkness. W. H. Ross found that ferric sulphate soln. are reduced to ferrous sulphate by exposure to **ultra-violet light**, and the action is greater if sugar be present. The reaction was studied by R. Audubert, A. Klemenc and H. F. Hohn. A. Kailan observed that acidic or neutral soln. of ferric sulphate are reduced to ferrous sulphate, in the presence or absence of sugar, by exposure to **radium rays**. G. L. Clark and L. W. Pickett observed no perceptible change when ferric sulphate is exposed to the **X-rays**; and A. Hébert and G. Reynaud measured the absorption of X-rays by aq. soln. of the salt. G. Reboul and E. Bodin, and E. Bodin found that rays capable of ionizing gases are emitted from pastilles of powdered, anhydrous ferric sulphate when traversed by an electric current.

L. R. Ingersoll found the **magnetic rotatory power**, i.e. the sp. magnetic rotation

of the plane of polarization,  $\omega$ , for a soln. of sp. gr. 1.446 at 23°, and in a field of 12,050 gauss, for light of wave-length 12,500, 10,000, and 8000 Å. is respectively 0.0016, 0.0020, and 0.0029. C. E. Richards and R. W. Roberts observed that the magnetic rotatory power of soln. of ferric sulphate is positive, whilst the effect due to the salt is negative. There are two magnetic absorption spectral bands, one at 0.53 $\mu$ , and the other at 0.57 $\mu$ . The magnetic absorption spectra of chloride and sulphate are the same. E. Miescher, and F. Allison and E. J. Murphy studied the magneto-optic properties.

According to R. C. Wells, the eq. **electrical conductivity**,  $\lambda$ , of aq. soln. of ferric sulphate for an equivalent of the salt in  $v$  litres, is :

$v$	1.105	9.560	16.15	38.24	48.45	145.3	300.1	600.0
$\lambda$ { 0° .	13.30	24.69	—	38.4	—	—	76.0	95.0
25° .	24.89	45.32	—	73.2	—	—	—	—
30° .	26.24	—	59.50	—	89.50	145.7	—	—

The results show that at low dilutions, the conductivity is abnormally low, whilst at high dilutions it is abnormally high. As the dilution increases, a precipitate is produced, the rate of its formation increases enormously with a rise of temp. This all agrees with the assumption that ferric sulphate begins to undergo hydrolysis at a dilution of a few litres. G. Fousserau observed that the conductivity of the soln. increases with age; and G. Carrara and G. B. Vespignani found the eq. conductivities at 25° of fresh soln.,  $\lambda$ , and of soln. 24 hrs. old,  $\lambda'$ , were :

$v$	5	10	40	80	160	640	1280	2560
$\lambda$	36.93	47.69	67.04	99.28	127.28	225.92	298.24	404.48
$\lambda'$	—	48.61	82.88	124.64	196.64	348.16	360.96	422.40

Ferric sulphate suffers **hydrolysis** in aq. soln., but, as shown by M. Berthelot, and G. Fousserau, the aq. soln. of this salt in aq. soln. are in general more stable than is the case with aq. soln. of other ferric salts. The yellowish-brown soln. is strongly acid towards litmus, and on evaporation, it furnishes a brownish-yellow syrup, which, after a time, solidifies to a mass of indistinct crystals—partly white, partly pale yellow. The colourless octahedra reported by J. T. Cooper, and C. Sylvester, are, according to G. Forchhammer, more likely to have been ammonia or potash iron-alum. G. C. Wittstein found that the further evaporation of the soln. furnishes a brown resinous mass, which, when completely dehydrated is dirty white. If the resinous brown mass is mixed with water while still hot, it solidifies suddenly, and is more easily dried than before this treatment. According to T. Scheerer, the conc. aq. soln. does not become turbid when it is boiled, but the dil. aq. soln. do become turbid, and this the more the greater the dilution of the soln. The soln. also become turbid when boiled, and, the more dilute the soln., the lower the temp. required to produce a turbidity. A soln. with one part of the salt in 100 parts of water becomes turbid at 95°, and deposits about one-third of the solute as ferric sulphate; with 200 parts of water, the turbidity appears at about 70°, and about half the solute is deposited as ferric sulphate; with 400 parts of water, the corresponding data are 59° and three-fourths; with 800 parts of water, 50° and seven-eighths; and 1000 parts of water, 47.5° and nine-tenths. All this means that in aq. soln., ferric sulphate is hydrolyzed. Related observations were made by J. S. Anderson, S. U. Pickering, A. Recoura, R. Scharizer, E. A. Schneider, C. R. C. Tichborne, and F. Wirth and B. Bakke. According to U. Antony and G. Gigli, a clear neutral aq. soln. of ferric sulphate remains clear until highly diluted, when it becomes gradually turbid by the separation of the hydrogel of hydrated ferric oxide. During the hydrolysis basic salts are first formed, and these are ultimately converted into the insoluble hydroxide. The ferric sulphate is slowly re-formed on disturbing the state of equilibrium by adding potassium ferrocyanide, provided the soln. be not too dilute to allow of the dissolution of the hydrated ferric oxide in the sulphuric acid. F. K. Cameron and W. O. Robinson said that the precipitates—the so-called basic salts—have no well-defined composition; and U. Antony and

G. Gigli added that the hydrolysis is complete with a dilution of 1 : 60,000. According to G. Carrara and G. B. Vespignani, the degree of hydrolysis of a 22.3 per cent. soln., in the presence of hydrated ferric oxide, is 0.9 per cent. ; they also calculated, from observations on the hydrolysis of methyl acetate, that at 25°, 0.2N- $\text{Fe}_2(\text{SO}_4)_3$ , a month old, contains 1.33 grms. of  $\text{Fe}_2(\text{SO}_4)_3$  per 100 c.c. G. Wiedemann made observations on the percentage hydrolysis of these soln., and U. Antony and G. Gigli calculated for soln. containing grams of  $\text{Fe}_2(\text{SO}_4)_3$  per 100 c.c. of soln., aged for 10 days at 10°, the percentage hydrolysis :

$\text{Fe}_2(\text{SO}_4)_3$	:	:	6.7	2.0	1.0	0.50	0.10	0.050	0.025	0.0125
Hydrolysis	:	:	4	11	23	33	57	67	82	91 per cent.

R. C. Wells calculated for soln. with 6.67, 0.104, and 0.00651 grm.  $\text{Fe}_2(\text{SO}_4)_3$  per 100 c.c. at 25°, the percentage hydrolysis 0, 12, and 40.0 respectively ; he also inferred from his observations of the electrical conductivity of aq. soln. that the hydrolysis proceeds in two stages embodying a rapid change unaccompanied by precipitation, and a slower change progressing at a measurable rate and accompanied by the formation of a basic sulphate. The formation of the basic salt is greatly favoured by raising the temp., or diluting the soln.

F. Seidel, and D. Vorländer observed that soln. of ferric sulphate show the Tyndall effect ; A. Quartaroli observed that when a dil. soln. is centrifuged for some hours, differences in concentration can be detected. M. V. Dover observed that the hydrolysis is greater in light than in darkness. A. Krause found that the **H'-ion concentration** of 0.1N- $\text{Fe}_2(\text{SO}_4)_3$  is  $p_{\text{H}}=1.3$  ; on adding varying amounts of alkali—sodium or potassium-hydroxide, sodium or potassium carbonate, sodium hydrocarbonate, or aniline—to a fixed vol. of a soln. of ferric sulphate, the ratio  $\text{Fe}_2\text{O}_3 : \text{SO}_3$  of the precipitate is related to the  $p_{\text{H}}$ -value or the acidity of the soln. A precipitate free from sulphate is obtained only when  $p_{\text{H}} > 7.7$ . On adding the theoretical proportions of sodium hydroxide or carbonate, and aq. ammonia, the values of the  $\text{Fe}_2\text{O}_3 : \text{SO}_3$  ratio are respectively 24.0, 8.8, and 11.1. Ammonia in the more acidic soln. acts as a strong base—*vide infra*, the basic-ferric sulphates. G. S. Tilley and O. C. Ralston observed that soln. of ferric sulphate begin to hydrolyze when the H'-ion conc. is  $10^{-3}$  and the OH'-ion conc. is  $10^{-11}$ , whilst hydrolysis is ended when the H'-ion conc. is  $10^{-4}$ , and the OH'-ion conc. is  $10^{-10}$ . W. Manchot and co-workers made observations on the **solvation** or hydration of the mol. of ferric sulphate in aq. soln., and they calculated that in soln. with 0.6874 and 1.460 mols  $\text{Fe}_2(\text{SO}_4)_3$  per litre, at 25°, each mol. of  $\text{Fe}_2(\text{SO}_4)_3$  is loaded respectively with 39.9 and 27.8 mols. of  $\text{H}_2\text{O}$ . J. N. Brønsted and K. Volquartz studied the complex ions  $[\text{Fe}(\text{H}_2\text{O})_6]^{+++}$ .

The **electromotive force** of iron electrodes in electrolytes containing ferric sulphate has been discussed previously. M. le Blanc studied the **polarization** of sulphuric acid soln. of the two iron sulphates using electrodes of gold and platinum. L. Riéty measured the difference of potential exhibited by soln. of ferric sulphate passing through capillary tubes when under a press. of 25 atm. The **electrolysis** of aq. soln. of ferric sulphate has been discussed in connection with the electro-deposition of iron. The **cathodic reduction** of ferric sulphate to ferrous sulphate with an iron cathode was studied by H. Buff, N. Kameyama and K. Takahashi, and R. Kremann and co-workers, who obtained 96 to 97 per cent. reduction in 1.5N- $\text{Fe}_2(\text{SO}_4)_3$  using a cathodic current density of 1 amp. ; only a little iron was deposited. Z. Karaoglanoff observed that the presence of ammonium sulphate had no perceptible influence on the yield. He also found that the current which just produces an evolution of hydrogen at a platinum cathode immersed in a soln. of iron-alum in 2 minutes was found to be proportional to the conc. of the soln. ; it increases by about 3 per cent. of its value per degree rise of temp. The addition of some normal salts—*e.g.* copper sulphate, silver nitrate, mercuric chloride, and more feebly, zinc sulphate, and ammonium molybdate—to the soln. increases the value of the critical currents ; in the case of copper sulphate, for example, this is

due to the deposition of copper at the cathode; other salts have no action, and a few—stannic chloride, or stannic acid—diminish the critical currents; among these, the action of the chromates is probably due to the formation of a diaphragm of chromic oxide—with potassium chromate or dichromate, small proportions accelerate and large proportions retard the action. With smooth platinum, the critical current is proportional to the surface of the electrode, hence with platinized electrodes very much larger currents can be used. A horizontal cathode gives a larger value than a vertical one. Stirring the soln. has a very marked effect in increasing the critical current. A coulometer can be constructed on the basis of these results; the anode is enclosed in a porous pot near the surface of the soln. of iron-alum in which the platinized cathode is immersed and which is stirred by a current of carbon dioxide. The ferrous salt produced is titrated with a soln. of potassium permanganate. A. Klemenc observed that in electrolysis with a gas-cathode, the reduction of the ferric salt by the hydrogen is not dependent on the presence of a solid electrode. This reduction may be due to the electrons slowly discharged from the cathode, or else in accord with  $\text{Fe}^{++} + \text{H} \rightarrow \text{Fe}^{\cdot\cdot} + \text{H}^{\cdot}$ . F. Oettel studied the influence of the current density on the cathodic reduction of soln. of ferric sulphate; H. C. Allen, J. C. Hostetter, A. Klemenc, and E. Nietz discussed the reversal of the action by anodic oxidation; and A. Brochet and J. Petit, O. Collenberg and S. Bodforss, and F. Pearce and C. Couchet, the reduction of the soln. of ferric sulphate by alternating currents.

M. Faraday showed that anhydrous ferric sulphate is paramagnetic; J. Plücker studied the **magnetic properties**; and G. Berndt showed that no magnetic hysteresis can be perceived in a magnetic field of 200 gauss. P. Théodorides gave  $56.21 \times 10^{-6}$  mass unit for the **magnetic susceptibility** of the salt. T. Ishiwara, and K. Honda and T. Ishiwara found that with a field of 2000 gauss, the magnetic susceptibility was:

	-177.3	-130.4°	-60.2°	0.1°	23.1°	210.1°	493.2°	658.2°
$\chi \times 10^{-6}$	133.2	100.2	77.1	62.7	57.3	38.6	24.9	20.9

and for a preparation with the equivalent of three-sevenths of a mol. of water, in a field between 7000 and 17,000 gauss, H. K. Onnes and E. Oosterhuis obtained:

	-208.2°	-202.6°	-195.7°	-103.5°	16.7°
$\chi \times 10^{-6}$	177.1	167.3	157.2	85.6	53.3

The results are in general agreement with the rule  $\chi(T-\theta) = \text{constant}$ , where  $\theta$  denotes Curie's constant. The directions were discussed by R. Gans. H. K. Onnes and E. Oosterhuis showed that at low temp. the results are influenced by variations in the strength of the magnetic field.

M. Faraday showed that aq. soln. of ferric sulphate, not too dilute, are paramagnetic, but A. Quartaroli found that the diamagnetism of the water is approximately neutralized by the paramagnetism of the ferric sulphate when the soln. contains about 2.80 grms. of Fe per litre. Observations on the magnetic susceptibility of aq. soln. of ferric sulphate were made by E. Becquerel, H. Breternitz, J. Plücker, P. Théodorides, and G. Wiedemann. B. Cabrera and E. Moles found the susceptibility of soln. of ferric sulphate, at 20°, to be:

$\text{Fe}_2(\text{SO}_4)_3$	0.3508	0.4668	1.173	2.326	3.380	6.678	11.26	15.38
$\chi \times 10^{-6}$	0.5132	0.4439	0.0137	0.6989	1.3822	3.4541	6.4507	9.0020
$\chi_A \times 10^{-6}$	11,660	11,710	11,940	12,110	12,260	12,410	12,640	12,550

J. S. E. Townsend observed a linear relation between the dilution and the magnetic susceptibility of soln. at 10° in a field between 1 and 9 gauss. For the atomic susceptibility  $\chi_A$ , B. Cabrera and E. Moles gave the results indicated above. A. Quartaroli obtained for the mol. susceptibility,  $\chi_m$ , of soln. with a mol of  $\text{Fe}_2(\text{SO}_4)_3$  in  $v$  litres, at 18°:

$v$	10	20	50	100	250	500	750	1,000
$\chi_m \times 10^{-6}$	14,386	13,344	13,116	12,756	12,088	10,528	11,635	11,375

O. Liebknecht and A. P. Wills gave  $38 \times 10^{-6}$  mass unit for the susceptibility, or  $15,150 \times 10^{-6}$  for the mol. susceptibility, of an aq. soln. of ferric sulphate with 0.97 per cent.  $\text{Fe}_2(\text{SO}_4)_3$ , from which R. H. Weber calculated the at. susceptibility of the iron to be  $15,210 \times 10^{-6}$ , and J. S. E. Townsend gave  $75 \times 10^{-6}$  mass unit for the magnetic susceptibility at  $10^\circ$ . A. Heydweiller obtained  $37.9 \times 10^{-6}$  vol. unit for a soln. of sp. gr. 1.609 at  $10.8^\circ$  in a magnetic field of 0.181 to 1.13 gauss; and O. Wylach gave  $30.2 \times 10^{-6}$  vol. unit. B. Cabrera and E. Moles examined the effect of sulphuric acid on the susceptibility of soln. with 1.571 to 1.590 per cent. of  $\text{Fe}_2(\text{SO}_4)_3$  at  $20^\circ$  when the acid ratio indicates mols  $\text{H}_2\text{SO}_4$  : mols  $\text{Fe}_2(\text{SO}_4)_3$  :

Acid ratio .	0.0994	0.1989	0.3901	0.7752	1.2087	1.9998	2.4227	4.8477
$\chi \times 10^{-6}$ .	2.7535	3.0390	3.2180	3.7540	4.0043	4.2345	4.1424	4.3877

G. Wiedemann, R. H. Weber, B. Cabrera and E. Moles, and J. S. E. Townsend measured the effect of temp. on the magnetic susceptibility of aq. soln. of ferric sulphate; and it was found to decrease with a rise of temp. A. E. Oxley represented the susceptibility  $\chi$  at  $T^\circ \text{K.}$  by  $\chi = aT^{-1} + b$ , where  $a$  and  $b$  are constants. A. Heydweiller found that whilst the effect of variations in the strength of the magnetic field is imperceptible with small variations—say 0.18 to 1.1 gauss—yet over the range  $H=0.1$  to 40,000 gauss, the susceptibility changes about 30 per cent. Observations were also made by J. S. E. Townsend, O. Wylach, and R. H. Weber.

K. Honda and T. Ishiwara calculated the **magnetic moment** of a mol of  $\text{Fe}_2(\text{SO}_4)_3$  to be  $7.42 \times 10^{-20}$ , whilst H. K. Onnes and E. Oosterhuis' measurements gave  $10^{-20}$ . R. Gans calculated 3656 for the **magneton number** of anhydrous ferric sulphate, and P. Théodoridès, 28.97 between  $0^\circ$  and  $250^\circ$ , and 28.93 between  $70^\circ$  and  $550^\circ$ . Calculations from observations on aq. soln. were made by B. Cabrera and E. Moles, A. Quartaroli, R. H. Weber, and P. Weiss.

**The chemical properties of ferric sulphate.**—The reduction of soln. of ferric sulphate by nascent **hydrogen** follows similar lines to the case of ferric chloride. D. Tommasi noted that the salt is partially reduced by detonating gas. J. Eggert observed that in the absence of a catalyst no hydrogen was absorbed by a 0.1*N*-soln. of ammonium ferric sulphate; R. Böttger observed that nickel charged with hydrogen reduced the salt in soln. to ferrous sulphate; and similar results with palladium charged with hydrogen were obtained by W. Fresenius, W. H. Gintl, T. Graham, A. Hoenig, L. Kritschewsky, and K. I. Lissenko. The reduction with palladium charged with hydrogen was found by A. C. Chapman to be complete in 20 to 30 mins.; but W. H. Gintl found that by passing hydrogen into a boiling soln. of ferric sulphate, containing a piece of palladium, the reduction is very slow. S. Cooke, J. Eggert, and W. H. Gintl also found that a soln. of ferric sulphate is readily reduced by hydrogen in the presence of platinized platinum, or platinum sponge. J. H. Weibel studied the action of hydrogen under press. on the soln.

D. Florentin, M. Lachaud and C. Lepière, and F. Wirth and B. Bakke noted that anhydrous ferric sulphate is hygroscopic when exposed to **air**, but G. Keppeler and J. d'Ans found that if free sulphuric acid be absent, the salt is not particularly hygroscopic. J. Milbauer and O. Quadrat observed only a slight superficial change when the anhydrous sulphate is exposed in a current of dry air, but with moist air, water is rapidly absorbed forming, according to F. K. Cameron and W. O. Robinson, the decahydrate. A. Recoura found that when the white ferric sulphate is exposed to moist air it slowly forms the white and then the yellow enneahydrate; yellow ferric sulphate takes up water more rapidly than the white form producing the trihydrate. E. Posnjak and H. E. Merwin observed that both rhombic and hexagonal ferric sulphates slowly absorb water when exposed to air. For the action of air on the heated sulphate, *vide supra*.

The observations of J. S. Anderson, G. T. Gerlach, M. Lachaud and C. Lepière, and C. R. C. Tichborne show that anhydrous ferric sulphate is dissolved by **water**

very slowly, yielding a brown soln., and hence C. F. Bucholz, D. Florentin, and F. Ulrich wrongly thought that the solubility of the salt in water is very small. According to F. Wirth, 18.57 parts of water dissolve 81.43 parts. N. R. Dhar observed that the rate of solution of anhydrous ferric sulphate in water can be accelerated by the presence of a trace of the reducing agents—stannous chloride or ferrous sulphate, or of the enneahydrate, coquimbite. A. C. Oudemans also observed that the decahydrate, quenstedtite, is slowly dissolved by water. S. U. Pickering found that the rate of solution of the anhydrous sulphate in water is accelerated by raising the temp.; and L. C. A. Barreswil showed that the rate of solution of the anhydrous salt in water is considerably hastened if a little ferrous sulphate be present. G. Keppeler and J. d'Ans, and N. R. Dhar added that reducing agents like hydroxylamine, sulphur dioxide, and stannous chloride act similarly, presumably in consequence of the formation of some ferrous sulphate. A. Laurent, and A. Recoura reported that the anhydrous salt exists in at least three different molecular states distinguished by very different solubilities in water. It has been suggested that L. C. A. Barreswil's observation explains the results. A. Recoura's products were possibly contaminated with variable proportions of ferrous salts. M. Berthelot, and A. and P. Buisine inferred that the slowness of the process of dissolution of the anhydrous salt in water is due to the need for a preliminary hydration; and A. Recoura, a preliminary depolymerization of the salt. A. and P. Buisine observed that when stirred with a little water, the anhydrous sulphate sets as if it were a kind of plaster of paris. The hydrolysis of the salt in aq. soln. has been previously discussed. V. L. Bohnson studied the catalytic decomposition of **hydrogen dioxide** by ferric sulphate—*vide supra*, ferric chloride. H. Kwasnik found that an aq. soln. of ferric sulphate reacts with **barium dioxide** giving off oxygen, and forming hydrated ferric oxide—*vide* the action of ferric chloride on hydrogen dioxide.

K. H. Butler and D. McIntosh found that anhydrous ferric sulphate is not soluble in liquid **chlorine**. C. Hensgen observed that **hydrogen chloride** decomposes anhydrous ferric sulphate neither at ordinary temp., nor at 100°. L. C. A. Barreswil said that ferric sulphate is insoluble in conc. **hydrochloric acid**; and A. Recoura, that with boiling conc. hydrochloric acid, the acid salt  $\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$  is formed. O. Röhm obtained **ferric chlorosulphate**,  $\text{Fe}(\text{SO}_4)\text{Cl} \cdot 6\text{H}_2\text{O}$ , from a mixture of ferric chloride, sulphuric acid, and water in the mol. proportions 1 : 1 : 6; or from a mixture of ferric chloride and sulphate, and water in the mol. proportions 1 : 1 : 18. C. E. Schafhäütl observed that when a soln. of ferric sulphate is mixed with **sodium chloride**, it evolves hydrogen chloride at 60°, and if it be evaporated to dryness, and heated in air, chlorine is evolved, and a mixture of sodium sulphate and ferric oxide remains. E. Kothny also found that a dry mixture of ferric sulphate and sodium chloride gives off ferric chloride at 285°, but L. C. Jones and G. N. Terzieff found that if the mixture is heated in the presence of oxygen or air, chlorine is evolved. C. F. Schönbein observed that a mixture of ferric sulphate and **potassium iodide** reacts in the cold with the evolution of iodine, the reaction is vigorous when the mixture is warmed; no sulphur dioxide was formed. K. Seubert and R. Rohrer represented the reaction:  $2\text{Fe}_2(\text{SO}_4)_3 + 2\text{KI} = 2\text{FeSO}_4 + \text{K}_2\text{SO}_4 + \text{I}_2$ , where, according to K. Seubert and A. Dorrer, and E. I. Orloff, it is possible that **ferric iodosulphate**,  $\text{Fe}(\text{SO}_4)\text{I}$ , is formed as an intermediate product:  $(\text{FeSO}_4)_2\text{SO}_4 + 2\text{KI} = \text{K}_2\text{SO}_4 + 2\text{Fe}(\text{SO}_4)\text{I}$ , followed by  $2\text{Fe}(\text{SO}_4)\text{I} = 2\text{FeSO}_4 + \text{I}_2$ . O. Röhm, and B. Walther prepared what was regarded as ferric chlorosulphate,  $\text{Fe}(\text{SO}_4)\text{Cl} \cdot 6\text{H}_2\text{O}$ , by the action of chlorine on a soln. of ferrous sulphate, and from a soln. of equimolar parts of ferric chloride and sulphate. The salt has been used in the tanning industry. A. Skrabal, and E. Fleischer represented the action of **cuprous iodide** on a boiling soln. of ferric sulphate by:  $2\text{Fe}_2(\text{SO}_4)_3 + \text{Cu}_2\text{I}_2 = 2\text{CuSO}_4 + 4\text{FeSO}_4 + \text{I}_2$ . M. Hersch-kowitsch found that when a mixture of ferric sulphate and **potassium chlorate** is moistened and heated to 100°, chlorine dioxide mixed with a little chlorine is evolved. S. E. Moody observed that when a soln. of ferric sulphate is boiled with



**potassium iodate** and iodide, hydrolysis occurs:  $\text{Fe}_2(\text{SO}_4)_3 + 5\text{KI} + \text{KIO}_3 + 3\text{H}_2\text{O} = 2\text{Fe}(\text{OH})_3 + 3\text{K}_2\text{SO}_4 + 3\text{I}_2$ .

K. Brückner observed that when ferric sulphate is melted with **sulphur**, sulphur dioxide and iron sulphide are formed. Ferric sulphate—*vide supra*, ferric chloride—is reduced by **sulphur dioxide** or by a **sulphite** and a little mineral acid:  $\text{Fe}_2(\text{SO}_4)_3 + \text{SO}_2 + 2\text{H}_2\text{O} = 2\text{FeSO}_4 + 2\text{H}_2\text{SO}_4$ . The reducing action of a **thiosulphate** on ferric sulphate:  $2\text{Fe}^{+++} + 2\text{S}_2\text{O}_3^{--} = 2\text{Fe}^{++} + \text{S}_4\text{O}_6^{--}$ , was shown by J. T. Hewitt and G. R. Mann to be a tetramolecular reaction. The reaction was studied by J. Pinnow. According to L. C. A. Barreswil, ferric sulphate is insoluble in conc. **sulphuric acid**; and C. F. Bucholz found that the salt is soluble in aq. soln. of sulphuric acid, and when the soln. is evaporated, it furnishes a deliquescent, soluble, white powder—probably an acid sulphate. A. W. Davidson observed that ferric sulphate is very sparingly soluble in 100 per cent.  $\text{H}_2\text{SO}_4$ , and the suspension of ferric sulphate in 100 per cent.  $\text{H}_2\text{SO}_4$  gives neither the thiocyanate nor the prussian blue reaction. F. Wirth showed that 2·25N-, 6·685N-, and 19·84N- $\text{H}_2\text{SO}_4$  dissolve respectively 25·02, 14·50, and 0·05 grms.  $\text{Fe}_2(\text{SO}_4)_3$  per 100 grms. of soln. The equilibrium conditions in the system  $\text{Fe}_2\text{O}_3$ - $\text{SO}_3$ - $\text{H}_2\text{O}$  at different temp. have been previously discussed—Figs. 661 to 668. A number of acid salts have been reported. G. C. Weltzien, and A. Hoffmann reported  $\text{Fe}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  and  $\text{Fe}_2\text{O}_3 \cdot 6\text{SO}_3 \cdot 11\text{H}_2\text{O}$ , or  $\text{Fe}_2(\text{SO}_4)_3 \cdot 3\text{H}_2\text{SO}_4 \cdot 8\text{H}_2\text{O}$ ; but the equilibrium diagrams show with certainty the existence of  $\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3$  and of the ennea- and trihydrates. A. Hoffmann, A. Recoura, M. C. Schuyten, and P. Marguerite-Delacharlionny described hydrates with 1, 4, 8, and 12 mols. of water; but these do not appear on the equilibrium diagram.

J. A. Krenner found an acid ferric sulphate occurring with the other iron sulphates at Szomolnok, Hungary; its composition approximated that of **ferric tetrasulphate**,  $\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$ ; and it was called **rhomboclase**. R. Scharizer observed that the *enneahydrate* is the stable phase, at ordinary temp., with soln. containing 0·43 per cent.  $\text{Fe}_2\text{O}_3$ , 37·42 per cent.  $\text{SO}_3$ , and 62·15 per cent.  $\text{H}_2\text{O}$ . Expressing the proportions of these constituents in percentages, the enneahydrated tetrasulphate was found to be the stable phase with soln. within the following ranges of composition: W. P. Applebey and S. H. Wilkes gave 0·21 to 9·63 $\text{Fe}_2\text{O}_3$ , 40·64 to 31·88 $\text{SO}_3$ , and 59·15 to 58·49 $\text{H}_2\text{O}$  at 18°—*vide* Fig. 661; and at 25°, 0·25 to 8·0 $\text{Fe}_2\text{O}_3$ , 40 to 32·2 $\text{SO}_3$ , and about 59·8 $\text{H}_2\text{O}$ —*vide* Fig. 662. F. K. Cameron and W. O. Robinson gave 1·05 to over 10·87 $\text{Fe}_2\text{O}_3$ , 42·43 and below 31·35 $\text{SO}_3$ , and 56·52 to 57·78 $\text{H}_2\text{O}$  at 25°; and F. Wirth and B. Bakke, 3·53 to 9·39 $\text{Fe}_2\text{O}_3$ , 34·00 to 31·54 $\text{SO}_3$ , and 62·47 to 59·07 $\text{H}_2\text{O}$  at 25°. E. Posnjak and H. E. Merwin gave at 50°, 0·7 to 7·5 $\text{Fe}_2\text{O}_3$ , 57·00 to 33·0 $\text{SO}_3$ , and 42·3 to 59·5 $\text{H}_2\text{O}$ —Fig. 667; at 75°, 0·1 to 45·9 $\text{Fe}_2\text{O}_3$ , 55·5 to 35·51 $\text{SO}_3$ , and 46·4 to 59·90 $\text{H}_2\text{O}$ —Fig. 666; and at 110°, 0·3 to 1·0 $\text{Fe}_2\text{O}_3$ , 56·0 to 43·0 $\text{SO}_3$ , and 43·7 to 56·0—Fig. 665. The salt was obtained from sulphuric acid soln. of ferric sulphate by V. Komar, A. Recoura, R. Scharizer, G. McPhail Smith, R. F. Weinland and F. Ensgraber, and F. Wirth and B. Bakke. The mush of white or yellowish-white crystals is drained on a porous tile, washed with acetone or alcohol, and dried in air or over conc. sulphuric acid. R. Scharizer evaporated in air a soln. containing the mol. proportion  $\text{Fe}_2\text{O}_3 : \text{SO}_3 = 1 : 4$ , and obtained what he regarded as the *henahydrate*:  $\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 11\text{H}_2\text{O}$ ; this passed into the enneahydrate when kept over sulphuric acid for 24 hrs. He also said that the enneahydrate is obtained by treating the henahydrate with alcohol, or by evaporating the alcoholic soln. A. Recoura obtained the enneahydrate from a soln. of ferric sulphate in boiling conc. hydrochloric acid; and M. P. Applebey and S. H. Wilkes, from a sulphuric acid soln. of ferrous sulphate treated with nitric acid and evaporated in a desiccator. According to F. Wirth and B. Bakke, the fine powder is white, but the coarse powder is pale rose-red, and by contact with water, the salt forms yellowish-white needles. E. Posnjak and H. E. Merwin, R. Scharizer, and R. F. Weinland and F. Ensgraber found that under the microscope the crystals appear to be thin plates, and less

often they appear in aggregates of needles. J. A. Krenner said that rhomboclase occurs in clear, white, scaly crystals. R. Scharizer reported that the crystals are monoclinic with axial ratios  $a:b:c=0.4633:1:0.7416$ , and  $\beta=89^\circ 6'$ ; whilst E. Posnjak and H. E. Merwin showed that the crystals are rhombic, not monoclinic, and have the axial ratios  $a:b:c=0.563:1:0.940$ . The lozenge-shaped, tabular crystals have the base and pyramid as prominent forms, and unit prism and pinacoid are usually present. The basal or (001)-cleavage is marked, and there is a fibrous prismatic or (110)-cleavage. The optic axial angle  $2V$  is small, and the crystals are pleochroic—yellow in the directions  $\gamma$  and  $\beta$ , and purple in the  $\alpha$  direction. R. Scharizer observed that the birefringence is strong— $\mu_\gamma-\mu_\beta=0.099$ —but decreases slowly as the crystals are heated above  $70^\circ$ . The sp. gr. is 2.172 at  $16.4^\circ$ ; and the hardness is 2.0. The indices of refraction are  $\beta=1.551$ , and  $\gamma=1.650$ . E. Posnjak and H. E. Merwin gave for the indices of refraction:

	F-	Tl-	Na-	C-	Li-light
$\alpha$	1.545	1.538	1.533	1.529	1.528
$\beta$	1.564	1.556	1.550	1.545	1.544
$\gamma$	1.657	1.644	1.635	1.626	1.625

F. Wirth and B. Bakke showed that the enneahydrate quickly loses water on exposure to air, and R. Scharizer, and F. Wirth and B. Bakke found that when confined over sulphuric acid for about six months, 5 mols. of water are removed. R. Scharizer said that the enneahydrate loses 5 mols. of water at  $64^\circ$ . F. Wirth and B. Bakke found that 6 mols. of water are lost below  $98^\circ$ ; and A. Recoura observed that 6 mols. are lost between  $80^\circ$  and  $100^\circ$ . The remaining 3 mols. of water are driven off along with a mol. of  $\text{SO}_3$  at  $135^\circ$ , and anhydrous ferric sulphate remains. R. Scharizer thought that the *monohydrate*,  $\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot \text{H}_2\text{O}$ , is formed at  $128^\circ$ . A. Recoura also thought that the tetrasulphate passes into the normal, anhydrous sulphate when heated in conc. sulphuric acid to  $250^\circ$ . R. Scharizer tried to discriminate between the constitutional water, and the water of crystallization of the enneahydrate, and, instead of the formula:  $\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$ , he wrote:  $(\text{HO})_6\text{Fe}_2\text{S}_4\text{O}_{12} \cdot 6\text{H}_2\text{O}$ , or  $\{(\text{HO})\text{Fe}\}_2(\text{HSO}_4)_4 \cdot 6\text{H}_2\text{O}$ , or more simply  $\text{HO} \cdot \text{Fe}(\text{HSO}_4)_2 \cdot 3\text{H}_2\text{O}$ , or *ferric hydroxybishydrosulphate*. A. Recoura regarded the tetrasulphate as a dibasic acid, *ferrisulphuric acid*, which forms esters. It resembles chromosulphuric acid, but is more readily decomposed by water. When the tetrasulphate is dissolved in 96 per cent. alcohol, and the soln. is evaporated over conc. sulphuric acid, in vacuo, it furnishes a yellow, friable salt, *ethyl ferrisulphate*,  $\text{Fe}_2(\text{SO}_4)_3 \cdot (\text{C}_2\text{H}_5)_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ . R. F. Weinland and F. Ensgraber described a series of salts of what they called *disulphatoferric acid*,  $\text{H}[\text{Fe}(\text{SO}_4)_2] \cdot 4\text{H}_2\text{O}$ , or  $\text{HSO}_4 \cdot \text{Fe} : \text{SO}_4 + 4\text{H}_2\text{O}$ ; and R. Scharizer's formula:  $\text{Fe}(\text{OH})(\text{HSO}_4)_2$ , can be written as a hydroxydisulphatoferric acid,  $\text{H}_2[\text{Fe}(\text{OH})(\text{SO}_4)_2]$ , which furnishes salts like *sideronatrile*,  $\text{Na}_4\text{Fe}_2\text{S}_4\text{O}_{12} \cdot 7\text{H}_2\text{O}$ , or  $\text{Na}_2[\text{Fe}(\text{OH})(\text{SO}_4)_2] \cdot 3\text{H}_2\text{O}$ , and *römerite*,  $\text{RFe}_2\text{S}_4\text{O}_{16} \cdot 14\text{H}_2\text{O}$ —*vide infra*. R. Scharizer observed that the salt attracts moisture from the atmosphere, and dissolves undecomposed in the absorbed water; but F. Wirth and B. Bakke added that the salt is partially hydrolyzed by water vapour. R. Scharizer said that the aq. soln. is readily undercooled. M. P. Applebey and H. S. Wilkes found that the solubility of the salt in water is rapidly depressed by increasing the proportion of added sulphuric acid, and in the presence of 38 per cent.  $\text{SO}_3$ , the salt is almost insoluble at  $18^\circ$ , and likewise in the presence of 40 per cent.  $\text{SO}_3$  at  $25^\circ$ . The hydrolysis was studied by M. P. Applebey and S. H. Wilkes, A. Recoura, and R. Scharizer. When diluted or heated, the aq. soln. shows the same colour-changes as those exhibited by the normal sulphate; the mol. lowering of the f.p. is the additive result of the values for the components; R. Scharizer found that the hydrolysis of the salt in aq. soln. furnishes the basic salt copiapite,  $\text{Fe}_4\text{S}_5\text{O}_{21} \cdot 48\text{H}_2\text{O}$ ; the hydrolysis is prevented by sulphuric acid; and F. Wirth and B. Bakke found that at  $25^\circ$ , the presence of more than 1:6.699 acid is necessary for the salt to be stable—*vide supra*. R. Scharizer observed that the enneahydrate dissolves slowly in alcohol; and it is less soluble

in that menstruum than is copiapite or coquimbite; and F. Wirth and B. Bakke added that 100 grms. of a sat. soln. of the salt in alcohol, at 25°, contain 8 grms.  $\text{Fe}_2\text{O}_3$  and 17.18 grms.  $\text{SO}_3$ . A. Recoura said that with 90 per cent. alcohol, the complex:  $\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot (\text{C}_2\text{H}_5)_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ , is formed. R. Scharizer observed that acetone extracts sulphuric acid from the salt.

E. Posnjak and H. E. Merwin observed that small needles of a trihydrate,  $\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 3\text{H}_2\text{O}$ , are stable in soln. with the percentage proportions: 0.07  $\text{Fe}_2\text{O}_3$ , 75.37 to 57.0  $\text{SO}_3$ , and 24.56 to 42.3  $\text{H}_2\text{O}$  at 50°; 0.07 to 0.1  $\text{Fe}_2\text{O}_3$ , 74.14 to 55.5  $\text{SO}_3$ , and 25.79 to 44.4  $\text{H}_2\text{O}$  at 75°; and 0.06 to 0.3  $\text{Fe}_2\text{O}_3$ , 72.5 to 56.0  $\text{SO}_3$ , and 27.44 to 43.7  $\text{H}_2\text{O}$  at 110°. It is stable in contact with its aq. soln. up to 140°—Figs. 661 to 667. R. Scharizer said that at 10°, the trihydrate is stable in contact with soln. containing over 67 per cent.  $\text{H}_2\text{SO}_4$ ; and F. Wirth and B. Bakke thought that it might be present in soln. with 3.53  $\text{Fe}_2\text{O}_3$ , 34.00  $\text{SO}_3$ , and 62.47  $\text{H}_2\text{O}$  at 25°. R. Scharizer, and F. Wirth and B. Bakke observed that the trihydrate is formed, as indicated above, when the enneahydrate is kept over conc. sulphuric acid for some months, or, according to R. Scharizer, and A. Recoura, by heating the enneahydrate between 64° and 100°. A. Recoura also prepared a salt which may have been the trihydrate, or a ferrisulphuric acid, by adding 3 mols of sulphuric acid to a conc. soln. of a mol of ferric sulphate. The brown soln. gradually becomes colourless and deposits a white powder. The same product is obtained when the proportion of sulphuric acid is varied. J. Poizat studied the action of this salt on hydrogen dioxide. R. Scharizer said that the trihydrate forms thin, pale red plates or tabular monoclinic crystals; and E. Posnjak and H. E. Merwin observed that the crystals appear in the form of fine needles. R. Scharizer said that the crystals are biaxial, and that the optical character is feebly negative. The sp. gr. is 2.549. When exposed to air, water is absorbed and a skin of the enneahydrate is formed on the crystals. A. Recoura found that the trihydrate dissolves slowly in water. I. S. Teletoff and V. M. Simonova, and J. Poizat studied its action on hydrogen dioxide. H. Ungemach described the mineral **leucoglaukite**,  $\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 5\text{H}_2\text{O}$ , from Tierra Amarilla, Chili, with pale blue, hexagonal crystals with  $a:c=1:0.5589$ .

In 1823, G. Forchhammer reported a compound of ferric oxide, **ammonia**, and sulphuric acid. According to G. Gore, H. McKee Elsey, and E. C. Franklin and

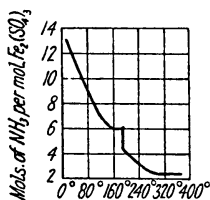


FIG. 671. — Thermal Dissociation of the Ammines of Ferric Sulphate.

C. A. Krause, anhydrous ferric sulphate is insoluble in liquid ammonia. F. Ephraim, and F. Ephraim and S. Millmann studied the ammines of ferric sulphate. A mol. of anhydrous ferric sulphate can absorb about 13 mols. of ammonia to form a voluminous, brown mass, which suffers no perceptible change on standing 16 hrs. in liquid ammonia. The product formed below 0° corresponds approximately with **ferric dodecamminesulphate**,  $\text{Fe}_2(\text{SO}_4)_3 \cdot 12\text{NH}_3$ ; at temp. between 20° and 160°, Fig. 671, it breaks down into **ferric hexamminesulphate**,  $\text{Fe}_2(\text{SO}_4)_3 \cdot 6\text{NH}_3$ ; and this in turn at temp. between 193° and 198°, furnishes **ferric tetramminesulphate**,  $\text{Fe}_2(\text{SO}_4)_3 \cdot 4\text{NH}_3$ ; and between 200° and 300°, the tetrammine yields **ferric diamminesulphate**,  $\text{Fe}_2(\text{SO}_4)_3 \cdot 2\text{NH}_3$ . G. Spacu obtained ferric octamminesulphate,  $\text{Fe}_2(\text{SO}_4)_3 \cdot 8\text{NH}_3 \cdot 4\text{H}_2\text{O}$ , or  $[(\text{H}_2\text{O})_2\text{Fe}(\text{NH}_3)_4]_2(\text{SO}_4)_3$ , by exposing powdered enneahydrated ferric sulphate to the action of dry ammonia. The dark reddish-brown, amorphous powder loses a part of its ammonia when exposed to air; it is insoluble in water, but is gradually hydrolyzed in contact with that liquid; it is soluble in dil. sulphuric acid; somewhat soluble in acetic acid; and insoluble in carbon disulphide, toluene, xylene, methyl, ethyl, and amyl alcohols, and in ether, acetone, chloroform, aniline, and pyridine. H. W. Kohlshütter studied the reaction:  $\text{Fe}_2(\text{SO}_4)_3 \cdot 3\text{cryst.} + 6\text{NH}_4\text{OH}_{\text{soln.}} = \text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O} + 3(\text{NH}_4)_2\text{SO}_4 + m\text{H}_2\text{O}$ .

T. W. B. Welsh and J. H. Broderson found that ferric sulphate is soluble in dry

**hydrazine**, and the soln. is decomposed by sodium with the precipitation of iron. T. Curtius and F. Schrader observed that hydrazine hydrate reduces a soln. of ferric sulphate rapidly to the ferrous state, and if an excess is added, green ferrous hydroxide is precipitated. E. J. Cuy also studied the reaction. T. Curtius and J. Rissom, and L. M. Dennis and A. W. Browne noted that **sodium azide** with a soln. of ferric sulphate gives blood-red ferric azide. W. Manchot and co-workers observed that soln. of ferric sulphate containing 0, 26.390, and 52.781 grms. of  $\text{Fe}_2(\text{SO}_4)_3$  per 100 c.c. absorb respectively 53.3, 25.9, and 13.1 c.c. of **nitrous oxide** per 100 c.c. of soln. W. Manchot showed that a soln. of ferric sulphate in 90 per cent. sulphuric acid dissolves **nitric oxide** forming a red soln. considered to be **ferric tetranitrosylsulphate**,  $\text{Fe}_2(\text{SO}_4)_3 \cdot 4\text{NO}$ . J. Napier observed that **arsenic** is attacked by a soln. of ferric sulphate. A soln. of ferric sulphate is reduced by **arsenic trioxide** to the ferrous state. J. Napier observed that, unlike the case with ferric chloride, neutral soln. of ferric sulphate, cold or hot, do not dissolve very much **antimony**. J. Hanus observed that when ferric sulphate is heated with **antimony trisulphide** the reaction may be symbolized:  $\text{Sb}_2\text{S}_3 + 5\text{Fe}_2(\text{SO}_4)_3 + 8\text{H}_2\text{O} = 2\text{H}_3\text{SbO}_4 + 10\text{FeSO}_4 + 5\text{H}_2\text{SO}_4 + 3\text{S}$ . J. Napier found that neutral soln. of ferric sulphate dissolve some bismuth; and L. L. de Koninck showed that an acidic soln. dissolves some **bismuth** and is simultaneously reduced to ferrous sulphate. K. Someya found that in an atm. of carbon dioxide, an acidified soln. of ammonium ferric sulphate is reduced quantitatively by **bismuth amalgam**; and if a molybdenum salt is present as catalyst, the reduction proceeds quantitatively in air. J. Hanus represented the reaction with **bismuth trisulphide**:  $\text{Bi}_2\text{S}_3 + 3\text{Fe}_2(\text{SO}_4)_3 = 6\text{FeSO}_4 + \text{Bi}_2(\text{SO}_4)_3 + 3\text{S}$ .

C. F. Schönbein, and E. Heymann and co-workers said that soln. of ferric sulphate are completely reduced by powdered **carbon**, but P. Rona and L. Michaelis observed only a slight reduction, and they added that the charcoal adsorbs the  $\text{Fe}^{+++}$ -ions but not so readily as is the case with  $\text{Hg}^{++}$ -ions or  $\text{Ag}^+$ -ions. J. H. Weibel studied the action of **carbon monoxide** on soln. of the salt. W. Manchot and co-workers found that soln. containing 0, 26.390, and 52.781 grms.  $\text{Fe}_2(\text{SO}_4)_3$  per 100 c.c. of soln. absorb respectively 95.7, 45.8, and 22.7 c.c. of **acetylene** per 100 c.c. According to A. Recoura, 96 per cent. **alcohol** dissolves the white form of anhydrous ferric sulphate in many months, the yellow form in 3 or 4 days, and the white modification of the enneahydrate in about a month; and the soln., in vacuo, deposits the complex:  $\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 2\text{C}_2\text{H}_5\text{OH} \cdot 2\text{H}_2\text{O}$ . The yellow form of the enneahydrate dissolves in 96 per cent. alcohol in 24 hrs. forming the soluble acid sulphate,  $\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3$ , and the insoluble basic sulphate,  $6\text{Fe}_2(\text{SO}_4)_3 \cdot \text{Fe}_2\text{O}_3$ ; the salt dissolves in absolute alcohol without decomposition. The red alcoholic soln. of ferric sulphate when exposed in a closed vessel to light was found by T. von Grotthus to be slowly reduced to a pale yellow soln. containing ferrous sulphate, but in darkness no change was observed. E. Müller and O. Diefenthaler observed no perceptible reduction occurred when an alcoholic soln. containing hydrochloric acid was heated. A. W. Davidson observed that the salt is insoluble in **acetic acid**. The salt is precipitated from its aq. soln. by acetic acid; and A. Recoura prepared a complex salt by the action of **acetic anhydride** on the enneahydrate. A. Naumann and M. Hamers, and M. Hamers found that ferric sulphate is insoluble in dry **methyl** or **ethyl acetate**, or in ethyl acetate sat. with water at  $18^\circ$ ; A. Naumann and W. Eidmann, and W. Eidmann, that the salt is insoluble in **acetone**; A. Conduché, that when ferric sulphate is heated in **chloroform**, ferrous and ferric chlorides are formed; G. Lemoine, that when ferric sulphate is mixed with **oxalic acid** and heated, carbon dioxide is evolved, and ferrous sulphate is formed—water accelerates the reaction; and S. Hakomori studied the action of oxalic acid, of **citric acid**, and of **malic acid**. G. Spacu showed that the salt forms a complex,  $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{C}_6\text{H}_5\text{NH}_2 \cdot 6\text{H}_2\text{O}$ , with **aniline**; A. Naumann and J. Schröder, and J. Schröder, that the salt is insoluble in **pyridine**; G. Spacu, that it forms complexes with pyridine; H. McKee Elsey, that it is insoluble in **methylamine** and **ethyl-**

**amine**; and F. Blau, that it forms complex salts with *aa'*-**dipyridyl** and with *α*-**phenanthroline**. G. Fuseya and co-workers detected complex cation formation with **glycine**. F. Rohart observed that ferric sulphate is adsorbed from its aq. soln. by **animal or vegetable substances**, and this so tenaciously, that it cannot be extracted by hydrochloric acid, and it does not give a precipitate of barium sulphate when digested with a boiling soln. of barium chloride. Meat treated with ferric sulphate retains its red colour, and becomes hard enough to resist scratching by the finger-nail.

According to C. G. Schluederberg, and J. Napier, **copper** is readily dissolved by a soln. of ferric sulphate, and the action is not affected by light. The surface action on the copper is almost instantaneous so that the observed speed of dissolution is governed by the rate of stirring. The reaction was studied by D. Nishida, and S. A. Pletenew and W. N. Rosow. L. Gmelin stated that on boiling a soln. of ferric sulphate with **silver**, ferrous and silver sulphates are formed, but, as the liquid cools, the silver is again precipitated, and ferric sulphate re-formed—*vide supra*, the action of silver sulphate on ferrous sulphate. According to P. C. McIlhiney, when **gold** is dissolved by hydrochloric acid in the presence of a ferric salt, the latter acts as a carrier of chlorine. J. Napier studied the action. Z. Roussin found that an acidified soln. of ferrous sulphate is rapidly reduced by **magnesium** forming ferrous sulphate, and some iron which appears as a black film on the magnesium, and which soon dissolves. The reaction was studied by A. Hoenig, and W. N. Hartley. A. W. Beshgetoor said that no iron is formed if too great an excess of acid is not present and the soln. is cooled. T. E. Thorpe, and S. Sugden observed that the reducing action is favoured by a rise of temp., and an increasing concentration of the ferric salt and is retarded by reducing the concentration of sulphuric acid. J. Napier found that the soln. is also reduced by **zinc**, and **cadmium**; and A. Hoenig, S. Sugden, and T. E. Thorpe said that the reaction resembles the case with magnesium—*vide ferric chloride*. L. W. McCay and W. T. Anderson represented the reaction between **mercury** and a soln. of ferric sulphate to which sulphuric acid has not been added, by the equation:  $\text{Fe}_2(\text{SO}_4)_3 + \text{Hg} \rightleftharpoons 2\text{FeSO}_4 + \text{HgSO}_4$ . The reduction is complete in the presence of hydrochloric or sulphuric acid and an equivalent amount of alkali chloride. D. Borar observed that in the absence of hydrochloric acid, mercury does not reduce a soln. of iron-alum. P. C. Ray showed that the presence of a trace of ferric sulphate retards the dissolution of mercury in nitric acid. K. Masuda studied the reduction of the soln. by **zinc amalgam**. A. Hoenig observed that ferric sulphate in soln. is completely reduced to ferrous sulphate by **aluminium**, and, as in the case of zinc and magnesium, a black film of iron forms on the metal. The reaction was also studied by W. Scott, and by W. Heller. J. Napier found that a neutral soln. of ferric sulphate is readily reduced by **tin** as the tin passes into solution; the action is hastened by heat. I. A. Lösner also found that a sat. soln. of ferric sulphate rapidly dissolves tin. J. Napier showed that a neutral soln. of ferric sulphate dissolves **lead** and is itself reduced to ferrous sulphate, but a protective film of lead sulphate is formed on the metal. By raising the temp. of the soln., more lead dissolves and some hydrated ferric oxide is precipitated. A soln. of iron-alum, acidified by sulphuric or hydrochloric acid, was found by K. Someya to be completely reduced to ferrous salt by **lead amalgam**. C. L. Berthelot, J. Napier, A. and P. Buisine, and J. J. Berzelius observed that when a soln. of ferric sulphate is digested with **iron filings**, ferrous sulphate is formed, hydrogen is evolved, and a basic ferric sulphate is precipitated. T. E. Thorpe, and J. C. Essner found that, unlike the case with zinc and magnesium, the reducing action is reduced by raising the temp. of the acidified soln. I. A. Lösner observed that iron is scarcely attacked by a sat. soln. of ferric sulphate; A. Hutin utilized the reaction:  $\text{Fe}_2(\text{SO}_4)_3 + \text{Fe} = 3\text{FeSO}_4$ , in the preparation of green vitriol. J. C. Essner observed that in dil. soln., the rate of reduction of ferric to ferrous sulphate by iron is increased if platinum be present. J. Napier found that the

soln. is reduced by **cobalt**, and by **nickel**, but not by **platinum**. R. Böttger reported that **palladium**, not charged with hydrogen, will reduce a soln. of ferric sulphate to the ferrous state.

A. Vesterberg found that when a conc. soln. of **sodium hydroxide** acts on anhydrous ferric sulphate, a crystalline powder of  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$  is formed. A. Krause studied the action of alkali hydroxides and carbonates on soln. of ferric sulphate. E. Kothny found that anhydrous ferric sulphate reacts slowly with **copper oxide** at  $300^\circ$  to  $600^\circ$ , in accord with  $3\text{CuO} + \text{Fe}_2(\text{SO}_4)_3 \rightleftharpoons 3\text{CuSO}_4 + \text{Fe}_2\text{O}_3$ ; between  $500^\circ$  and  $550^\circ$ , the state of equilibrium is such that a third of the total copper is soluble in water. F. Thomas, A. Elliott, and C. Millberg found that copper oxide or **copper hydroxide** dissolves in a soln. of ferric sulphate more rapidly than is the case with cuprous oxide, and, added M. de K. Thompson, if an excess of copper oxide is present, a basic salt is formed. J. D. Sullivan and G. L. Oldright found that acidified soln. of ferric sulphate dissolve particles of **cuprous oxide**, or **cuprite**, of 3's mesh in size in 8 days, and in 3 days 99 per cent. is dissolved. Particles less than 100's mesh dissolve completely in an hour. Oxygen is necessary for complete soln. F. Thomas, and C. Millberg represented the reaction:  $3\text{Cu}_2\text{O} + 4\text{Fe}_2(\text{SO}_4)_3 = 6\text{CuSO}_4 + 6\text{FeSO}_4 + \text{Fe}_2\text{O}_3$ ; and if an excess of sulphuric acid is present, L. L. de Koninck gave  $\text{Cu}_2\text{O} + \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{SO}_4 = 2\text{CuSO}_4 + 2\text{FeSO}_4 + \text{H}_2\text{O}$ . M. de K. Thompson said that it is probable that the cuprous oxide is first oxidized to cupric oxide before it dissolves. J. A. Hedvall and J. Heuberger observed that anhydrous ferric sulphate begins to react with **calcium oxide** at  $584^\circ$  and the reaction:  $3\text{CaO} + \text{Fe}_2(\text{SO}_4)_3 = 3\text{CaSO}_4 + \text{Fe}_2\text{O}_3$  is vigorous at  $620^\circ$ ; the thermal value of the reaction is 61.1 Cals.: the reaction begins with **strontium oxide** at  $410^\circ$ , proceeds vigorously at  $510^\circ$ , and has the thermal value 165.1 Cals.; and the reaction with **barium oxide** begins at  $338^\circ$ , proceeds vigorously at  $470^\circ$ , and has the thermal value 199.2 Cals. D. Balareff discussed the part played by moisture in the reaction. J. A. Hedvall and J. Heuberger found that with barium hydroxide, a reaction occurs slowly at  $350^\circ$  to  $395^\circ$ . G. Keller noted that limonite is formed when **calcite** is treated with soln. of ferric sulphate—*vide supra*, ferrous sulphate. H. Schopper studied the precipitation of ferric hydroxide from soln. of the sulphate by quicklime, or limestone, and J. N. von Fuchs, J. von Kobell, and H. Demarçay observed that the alkaline earths, **magnesium, manganese, zinc, and copper carbonates**, precipitate hydrated ferric oxide from a soln. of ferric sulphate. A. Mailhe found that when **mercuric oxide** is added to a soln. of ferric sulphate, a lemon-yellow powder of  $\text{HgSO}_4 \cdot 2\text{HgO}$  is formed; E. A. Schneider also found that with **aluminium hydroxide** at ordinary temp., the iron may all be precipitated as a basic salt, particularly from the boiling soln. C. Fahlberg, L. Lucas, C. Semper and C. Fahlberg, and E. Sack observed that a neutral soln. of ferric sulphate deposits all the iron as hydrated oxide when it is treated with **lead dioxide**. M. K. Hoffmann, and C. Friedheim and M. K. Hoffmann found that **molybdenum dioxide** is oxidized to the trioxide by ferric sulphate soln.:  $\text{MoO}_2 + \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O} = \text{MoO}_3 + 2\text{FeSO}_4 + \text{H}_2\text{SO}_4$ . Hydrated ferric oxide is completely precipitated from a soln. of ferric sulphate by **manganese dioxide**, and the reaction was employed by J. W. Kynaston, and P. and F. M. Spence for purifying ferruginous alumina; and by C. Marchal and J. Wiernik, for separating iron from chromium and aluminium. M. Geloso and co-workers, L. S. Lévy, and P. Nicolardot and co-workers studied the adsorption of ferric sulphate soln. by freshly-precipitated manganese dioxide, and the effect of copper and nickel sulphates on the adsorption. G. Kreimer studied the preferential absorption of ferric sulphate from soln. of aluminium sulphate. M. P. Applebey and S. H. Wilkes, F. K. Cameron and W. O. Robinson, A. Maus, S. U. Pickering, R. Scharizer, and F. Wirth and B. Bakke studied the solution of **ferric hydroxide**, and of **ferric oxysulphates** in aq. soln. of ferric sulphate.

The action of **alkali sulphides** on the soln. of ferric sulphate is discussed in connection with the reactions of analytical interest. F. Thomas, and C. Millberg found that **cuprous sulphide** is readily dissolved by a soln. of ferric sulphate:

$\text{Cu}_2\text{S} + 2\text{Fe}_2(\text{SO}_4)_3 = 2\text{CuSO}_4 + 4\text{FeSO}_4 + \text{S}$ ; and similarly with **cupric sulphide**,  $\text{CuS} + \text{Fe}_2(\text{SO}_4)_3 = \text{CuSO}_4 + 2\text{FeSO}_4 + \text{S}$ , and the dissolution of cuprous sulphide is favoured by the presence of ferrous sulphate. The thermal value of the above-mentioned reaction with cuprous sulphide was found by S. H. Emmens to be 15.15 Cals. The reaction was studied by J. D. Sullivan, H. E. Keyes, and G. D. van Arsdales. J. Hanus, and P. P. Budnikoff and K. E. Krause added that both reactions are incomplete and probably oxysulphides are formed. L. Whitby found that at ordinary temp. the reaction in acidic soln. can be symbolized:  $\text{Cu}_2\text{S} + \text{Fe}_2(\text{SO}_4)_3 = \text{CuS} + \text{CuSO}_4 + 2\text{FeSO}_4$ , but with a prolonged action, the reaction follows the course:  $\text{CuS} + \text{Fe}_2(\text{SO}_4)_3 = \text{CuSO}_4 + 2\text{FeSO}_4 + \text{S}$ . The reaction with an excess of acid, at  $60^\circ$  to  $80^\circ$ , also follows the course of the preceding equation. M. de K. Thompson observed that the action does not occur with cuprous sulphide when air (or oxygen) is excluded. The artificial and natural complex iron and copper sulphides were found by F. Thomas to be very slowly attacked by a soln. of ferric sulphate. P. P. Budnikoff and K. E. Krause represented the quantitative reaction with **calcium sulphide**:  $\text{CaS} + \text{Fe}_2(\text{SO}_4)_3 = \text{CaSO}_4 + 2\text{FeSO}_4 + \text{S}$ ; and S. H. Emmens found that the thermal value of the reaction with **zinc sulphide** is 25.94 Cals. J. Hanus found the analogous reaction with **mercuric sulphide** is incomplete, but the reactions with **stannous sulphide**, and **lead sulphide** are complete. S. H. Emmens gave 14.80 Cals. for the thermal value of the reaction with lead sulphide. G. de Bechi and co-workers utilized the reaction in the treatment of zinc-lead ores. E. Crepaz found that **potassium molybdenum cyanosulphide** is oxidized by ferric sulphate with the separation of sulphur. E. T. Allen and co-workers found that **marcasite** and **pyrite** are attacked by a soln. of ferric sulphate forming ferrous sulphate, sulphuric acid, and sulphur; E. Kothny observed that pyrite is slowly attacked by anhydrous ferric sulphate at  $290^\circ$ , and L. L. de Koninck showed that in a sealed tube with pyrite, and sulphuric acid, at  $170^\circ$ , iron-alum is reduced to ferrous sulphate. S. H. Emmens represented the reaction with **ferrous sulphide**, in aq. soln. of ferric sulphate:  $\text{FeS} + \text{Fe}_2(\text{SO}_4)_3 = 3\text{FeSO}_4 + \text{S} + 30.85$  Cals.

According to A. Haswell, and C. Meinecke, the oxidation of **mercurous chloride** by an acid soln. of ferric sulphate:  $\text{Hg}_2\text{Cl}_2 + \text{Fe}_2(\text{SO}_4)_3 + 2\text{HCl} = 2\text{HgCl}_2 + 2\text{FeSO}_4 + \text{H}_2\text{SO}_4$ , is catalytically favoured by stannic chloride. M. Berthelot discussed the thermal value of admixture of soln. of ferric sulphate with soln. of **sodium, potassium, and ammonium sulphates**. A. Gorgeu found that when anhydrous ferric sulphate is melted with sodium sulphate in a current of dry carbon dioxide, crystalline ferric oxide, ferrosic oxide, iron, iron sulphide, alkali sulphite, and carbon may be produced. The adsorption of ferric sulphate from aq. soln. by precipitated **barium sulphate** was discussed by F. W. Küster and A. Thiel, J. W. Mellor, T. W. Richards and co-workers, and E. A. Schneider. Z. Karaoglanoff observed that barium sulphate is insoluble in a sulphuric acid soln. of ferric sulphate. E. Zintl and F. Schloffer showed that **chromous sulphate** reduces a sulphuric acid soln. of ferric sulphate to the ferrous state. L. C. A. Barreswil found that a soln. of **ferrous sulphate** rapidly dissolves anhydrous ferric sulphate.

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*Zeit. anorg. Chem.*, **79**, 362, 1913; F. Wirth and B. Bakke, *ib.*, **87**, 21, 1914; G. C. Wittstein, *Repert. Pharm.*, **63**, 223, 1838; L. Wöhler and M. Grunzweig, *Ber.*, **46**, 1590, 1913; L. and P. Wöhler and W. Plüddemann, *ib.*, **41**, 703, 1908; E. Wülfing, *Tschermak's Mitt.*, (2), **9**, 401, 1888; O. Wylach, *Untersuchungen über die Magnetisierungszahlen von Eisen und Mangansalzen*, Barmen, 1905; E. Zintl and F. Schloffer, *Zeit. angew. Chem.*, **41**, 958, 1928.

### § 46. The Basic Ferric Sulphates

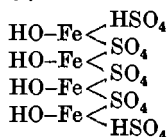
As indicated above, ferric sulphate is readily hydrolyzed, and although a great number of basic salts have been reported, either as laboratory products, or as minerals, less than half a dozen have been prepared under conditions where equilibrium between soln. and solid has been established, and at temp. between 50° and 200°. These basic salts are the heptadecahydrate,  $2\text{Fe}_2\text{O}_3 \cdot 5\text{SO}_3 \cdot 17\text{H}_2\text{O}$ , the mono- and pentahydrates,  $\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot \text{H}_2\text{O}$  and  $5\text{H}_2\text{O}$ , and the euneahydrate,  $3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$ . This work—Figs. 661 to 668—was done by E. Posnjak and H. E. Merwin,<sup>1</sup> F. K. Cameron and W. O. Robinson, M. P. Applebey and S. H. Wilkes, and F. Wirth and B. Bakke. A. Krause, as indicated above, studied the effect of alkalies on soln. of ferric sulphate, and he found that the composition of the precipitate at 15° changes with the OH<sup>-</sup>-ion conc. of the soln. Similar remarks apply to the complex salts of ferric sulphates so that there again basic salts are formed. The following list includes the basic ferric sulphates, and complex basic ferric sulphates which have been reported as minerals:

<i>Amarantite</i> (A. Frenzel, 1890)	$2\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot 7\text{H}_2\text{O}$
<i>Ammoniojarosite</i> (E. V. Shannon, 1929)	$(\text{NH}_4)_2\text{O} \cdot 3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 6\text{H}_2\text{O}$
<i>Apatelite</i> (A. Meillet, 1841)	$2\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}$
<i>Beaverite</i> (W. T. Schaller, 1912)	$\text{CuO} \cdot \text{PbO} \cdot \text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot 4\text{H}_2\text{O}$
<i>Bilinite</i> (J. Sebor, 1903)	$\text{FeO} \cdot \text{Fe}_2\text{O}_3 \cdot 24\text{H}_2\text{O}$
<i>Borgströmite</i> (M. Saxén, 1916)	$\text{Fe}_2\text{O}_3 \cdot \text{SO}_3 \cdot 3\text{H}_2\text{O}$
<i>Botryogen</i> (W. Haidinger, 1828)	$2\text{MgO} \cdot \text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 15\text{H}_2\text{O}$
<i>Butlerite</i> (C. Lausen, 1928)	$\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot 5\text{H}_2\text{O}$
<i>Carphosiderite</i> (A. Breithaupt, 1827)	$3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 10\text{H}_2\text{O}$
<i>Castanite</i> (L. Darapsky, 1890)	$\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot 7\text{H}_2\text{O}$
<i>Copiapite</i> (W. Haidinger, 1845)	$2\text{Fe}_2\text{O}_3 \cdot 5\text{SO}_3 \cdot 18\text{H}_2\text{O}$
$\beta$ - <i>Copiapite</i> (R. Scharizer, 1912)	$3\text{Fe}_2\text{O}_3 \cdot 8\text{SO}_3 \cdot 27\text{H}_2\text{O}$
<i>Clinocrocite</i> (S. Singer, 1879)	(See <i>clinophæite</i> )
<i>Clinophæite</i> (S. Singer, 1879)	$4(\text{K}, \text{Na})_2\text{O} \cdot \text{FeO}(\text{Fe}, \text{Al})_2\text{O}_3 \cdot 5\text{SO}_3 \cdot 8\text{H}_2\text{O}$
<i>Cubeite</i> (L. Darapsky, 1898)	$3\text{MgO} \cdot 2\text{Fe}_2\text{O}_3 \cdot 7\text{SO}_3 \cdot 3\text{H}_2\text{O}$
<i>Cyprusite</i> (P. F. Reinsch, 1882)	$(\text{Al}, \text{Fe})_2\text{O}_3 \cdot \text{SO}_3 \cdot 6\text{H}_2\text{O}$
<i>Ferronatrite</i> (J. B. Macintosh, 1906)	$3\text{Na}_2\text{O} \cdot \text{Fe}_2\text{O}_3 \cdot 6\text{SO}_3 \cdot 6\text{H}_2\text{O}$
<i>Fibroferrite</i> (H. Rose, 1833)	$\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot 10\text{H}_2\text{O}$
<i>Guildite</i> (C. Lausen, 1928)	$3(\text{Cu}, \text{Fe})\text{O} \cdot 2(\text{Fe}, \text{Al})_2\text{O}_3 \cdot 7\text{SO}_3 \cdot 17\text{H}_2\text{O}$
<i>Glockerite</i> (J. J. Berzelius, 1826)	$2\text{Fe}_2\text{O}_3 \cdot \text{SO}_3 \cdot 6\text{H}_2\text{O}$
<i>Hydroglockerite</i> (E. Greenley, 1919)	$2\text{Fe}_2\text{O}_3 \cdot \text{SO}_3 \cdot 8\text{H}_2\text{O}$
<i>Idrizite</i> (A. Schrauf, 1891)	$(\text{Mg}, \text{Fe})\text{O} \cdot (\text{Al}, \text{Fe})_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 16\text{H}_2\text{O}$
<i>Jarosite</i> (A. Breithaupt, 1852)	$\text{K}_2\text{O} \cdot 3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 6\text{H}_2\text{O}$
<i>Louderbackite</i> (C. Lausen, 1928)	$2\text{FeO} \cdot 3(\text{Fe}, \text{Al})_2\text{O}_3 \cdot 10\text{SO}_3 \cdot 15\text{H}_2\text{O}$
<i>Metavoltine</i> (J. Blaas, 1883)	$5(\text{K}_2, \text{Na}_2, \text{Fe})\text{O} \cdot 3\text{Fe}_2\text{O}_3 \cdot 20\text{SO}_3 \cdot 18\text{H}_2\text{O}$
<i>Paposite</i> (L. Darapsky, 1887)	$2\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 10\text{H}_2\text{O}$
<i>Pastreite</i> (L. Bergemann, 1866)	(See <i>raimondite</i> )
<i>Plagiocitrite</i> (S. Singer, 1879)	$(\text{K}, \text{Na})_2\text{O} \cdot 2\text{FeO} \cdot 3(\text{Al}, \text{Fe})_2\text{O}_3 \cdot 6\text{SO}_3 \cdot 27\text{H}_2\text{O}$
<i>Planoferrite</i> (F. Grünling, 1898)	$\text{Fe}_2\text{O}_3 \cdot \text{SO}_3 \cdot 15\text{H}_2\text{O}$
<i>Quetenite</i> (A. Frenzel, 1890)	$\text{MgO} \cdot \text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 13\text{H}_2\text{O}$
<i>Raimondite</i> (A. Breithaupt, 1866)	$2\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 7\text{H}_2\text{O}$
<i>Ransomite</i> (C. Lausen, 1928)	$\text{CuO} \cdot \text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 7\text{H}_2\text{O}$
<i>Römerite</i> (J. Grailich, 1858)	$\text{FeO} \cdot \text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 14\text{H}_2\text{O}$
<i>Rubrite</i> (L. Darapsky, 1890)	$\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot 3\text{H}_2\text{O}$
<i>Sideronatrite</i> (A. Raimondi, 1882)	$2\text{Na}_2\text{O} \cdot \text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 7\text{H}_2\text{O}$
<i>Slavikite</i> (R. N. C. R. Jirkorsky and F. Ulrich, 1926)	$(\text{Na}, \text{K})_2\text{O} \cdot 5\text{Fe}_2\text{O}_3 \cdot 13\text{SO}_3 \cdot 66\text{H}_2\text{O}$
<i>Utahite</i> (A. Arzruni, 1884)	$\text{Fe}_2\text{O}_3 \cdot \text{SO}_3 \cdot 2\text{H}_2\text{O}$
<i>Vegasite</i> (A. Knopf, 1913)	$\text{PbO} \cdot 3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 6\text{H}_2\text{O}$
<i>Voltaite</i> (J. Blaas, 1883)	$8\text{FeO} \cdot 2\text{K}_2\text{O} \cdot 3(\text{Fe}, \text{Al})_2\text{O}_3 \cdot 20\text{SO}_3 \cdot 46\text{H}_2\text{O}$

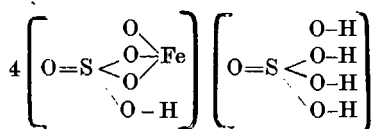
A. Recoura reported a product,  $7\text{Fe}_2\text{O}_3 \cdot 18\text{SO}_3 \cdot n\text{H}_2\text{O}$ , to be formed by the hydrolysis or evaporation of conc. soln. of ferric sulphate, but in all probability

it merely represents an uncompleted stage of the hydrolysis; there is no evidence of it in the equilibrium diagrams.

The yellow earth referred to in the first century as *μίον* by Dioscorides in his *Περὶ ὕλης ἰατρικῆς*, and as *misy*, by Pliny, in his *Historia naturalis*; and in the sixteenth century as *yellow atrament* by G. Agricola, is thought to refer partly to copiapite and partly to metavoltine. J. D. Dana suggested the term *misylite*, which H. Moissan mis-spells *migsite*. The mineral was described by J. G. Wallerius, J. F. L. Hausmann, A. Breithaupt, and H. Rose. E. F. Glocker called it *xanthosiderite*, and W. Haidinger, **copiapite**—from the locality Tierra Amarilla, near Copiapo, Chili, where the mineral was first found. It has been also reported from other localities—e.g. Knoxville, and Sulphur Bank, California; Rio Tinto, Spain; and Goslar in the Harz. Analyses were reported by G. Linck, C. Lausen, H. F. Collins, C. List, J. B. Macintosh, R. Jirkovsky, L. Darapsky, W. H. Melville and W. Lindgren, I. Domeyko, E. Manasse, W. T. Schaller, R. Scharizer, R. Mauzelius, H. Ahrend, T. L. Walker, W. J. McCaughey, J. F. Schairer and C. C. Lawson, and C. F. Rammelsberg. The results are best represented by the formula:  $2\text{Fe}_2\text{O}_3 \cdot 5\text{SO}_3 \cdot 18\text{H}_2\text{O}$ , or **ferric oxyptentasulphate**,  $\text{Fe}_4\text{O}(\text{SO}_4)_5 \cdot 18\text{H}_2\text{O}$ —P. Groth gave  $19\text{H}_2\text{O}$ ; E. Posnjak and H. E. Merwin,  $17\text{H}_2\text{O}$ ; and F. Wirth and B. Bakke,  $18\text{H}_2\text{O}$ . R. Scharizer's and W. T. Schaller's constitutional formulæ are as follows:



R. Scharizer's formula



W. T. Schaller's formula

R. Scharizer's formula,  $(\text{HO} \cdot \text{Fe})_4(\text{SO}_4)_3(\text{HSO}_4)_2 \cdot 15\text{H}_2\text{O}$ , is equivalent to a salt formed by the condensation of four mols. of ferrisulphuric acid,  $(\text{HO} \cdot \text{Fe})(\text{HSO}_4)_2$ , or **ferric hexahydroxyptentasulphate**.

Copiapite is the most conspicuous of the basic ferric sulphates; and it is the salt which first separates from an aq. soln. of ferric sulphate, and it can be recrystallized from its aq. soln. without an excess of sulphuric acid being present. R. Scharizer observed that it separates in sulphur-yellow crystals from soln. of ferric sulphate with the mol. ratio  $\text{SO}_3 : \text{Fe}_2\text{O}_3$  exceeding 2·5; if the ratio is just 2·5, then copiapite is formed alone; if it is between 2·5 and 3·0, the copiapite is mixed with enneahydrated ferric sulphate; and if the ratio is 3·0, the latter salt is alone produced. F. Wirth and B. Bakke observed that the salt is in equilibrium with a soln. at  $25^\circ$  when the soln. contains  $\text{Fe}_2\text{O}_3$ , 18·52 to 20·65 per cent.,  $\text{SO}_3$ , 26·80 to 27·96 per cent., and  $\text{H}_2\text{O}$ , 54·68 to 52·29 per cent. Here the mol. ratio  $\text{SO}_3 : \text{Fe}_2\text{O}_3$  is between 2·614 and 2·889. E. Posnjak and H. E. Merwin found that it is stable in contact with its sat. soln. only below  $90^\circ$ —*vide* Figs. 661 to 668.

R. Scharizer prepared what he called  $\beta$ -copiapite corresponding with **ferric hydroxytetrasulphate**,  $(\text{HO} \cdot \text{Fe})_4(\text{SO}_4)_4 \cdot 13\text{H}_2\text{O}$ ; and F. Wirth and B. Bakke added that it is in equilibrium at  $25^\circ$  with soln. in which the mol. ratio  $\text{Fe}_2\text{O}_3 : \text{SO}_3$  lies between 1 : 3·472 and 1 : 2·889. Ordinary copiapite was then called  $\alpha$ -copiapite. E. Posnjak and H. E. Merwin have shown that the evidence justifying the recognition of this product as a chemical individual is extremely unsatisfactory, and the only valid inference from the observed results is that equilibrium had not been established, and that the alleged  $\beta$ -copiapite is a mixture of copiapite and normal ferric sulphate. For the identity of *janosite* with copiapite, *vide infra*.

Copiapite occurs in nature as a sulphur-yellow or yellowish-brown incrustation, or in loose aggregates of crystalline scales, or granular masses. G. Linck said that the crystals are monoclinic, with the axial ratios  $a : b : c = 0 \cdot 47904 : 1 : 0 \cdot 97510$ , and  $\beta = 72^\circ 3'$ , but E. Bertrand, A. des Cloizeaux, Z. Toborffy, and E. Manasse said that the crystals are rhombic. C. Lausen said that the crystals of the copiapite occurring at Jerome, Arizona, are monoclinic. The crystals occur in thin, pseudo-

hexagonal plates parallel to (100). The pinacoid is at (100), the base at (001); they also occur in prisms elongated parallel to (001), and flattened parallel to (010). The (010)-cleavage is perfect, and the (100)-cleavage imperfect. E. Posnjak and H. E. Merwin also found that the pale greenish-yellow, artificial crystals are rhombic with the axial ratios  $a:b:c=0.81:1:-$ , and added that the crystals have a monoclinic appearance due to the unequal development of the boundaries which correspond with the crystal faces. The crystals of copiapite are usually tabular parallel to (010), and the (010)-cleavage is good. The crystals in the  $\alpha$ -direction are colourless; in the  $\beta$ -direction, light greyish-yellow; and in the  $\gamma$ -direction, bright yellow. A. Frenzel said that the green tinge of the crystals is a consequence of their exposure to sunlight, and that it disappears in darkness. The optical character is negative; the optical axial angle  $2V=52^\circ$ ; and, according to A. des Cloizeaux,  $2H_0=113^\circ 10\frac{1}{2}'$  for red-light, and  $2H_0=114^\circ 15'$  for yellow-light; and G. Linck gave  $2H_0=111^\circ 36'$  for yellow-light. G. Linck gave 2.103 for the sp. gr., and C. Lausen, 2.092. The hardness is 2.5. The crystals of copiapite attract moisture, and deliquesce more slowly than either rhomboclase or coquimbite. E. Manasse observed that when copiapite is confined over calcium chloride, it loses about 1.82 per cent. of water, *i.e.* about a mol., and this is thought to be hygroscopic or adsorbed water; R. Scharizer observed further that copiapite loses about 5 mols. of water at  $60^\circ$ ; 6 mols. at  $90^\circ$ , 12 mols. at  $116^\circ$ ; and at a higher temp. 3 more mols. are lost at  $200^\circ$ , and the remaining 2 mols. above  $200^\circ$ . Some results were:

	50°	60°	90°	100°	110°	130°	170°	200°	270°
Loss . .	1.31	7.98	9.18	14.12	17.31	20.90	24.25	25.98	28.50 per cent.

The dehydration curve has breaks at  $60^\circ$ ,  $90^\circ$ , and  $120^\circ$ . There is a marked change in vol. at about  $100^\circ$  when the colour changes from sulphur-yellow to brownish-yellow; it melts in its water of crystallization at  $112^\circ$ . G. Linck's studies on the dehydration are in agreement with those of R. Scharizer. E. Posnjak and H. E. Merwin found that the optical dispersion is small. E. Manasse reported that the indices of refraction of copiapite for Na-light ranged from  $\alpha=1.506$  to 1.509,  $\beta=1.529$  to 1.532, and  $\gamma=1.573$  to 1.577; W. J. McCaughey gave  $\alpha=1.525$ ,  $\beta=1.545$ , and  $\gamma=1.592$ ; E. S. Larsen,  $\alpha=1.510$  to 1.530,  $\beta=1.535$  to 1.550, and  $\gamma=1.575$  to 1.600; T. L. Walker,  $\beta=1.537$ , and  $\gamma=1.578$ ; C. Lausen,  $\alpha=1.525$ ,  $\beta=1.540$ , and  $\gamma=1.595$ ; and W. E. Ford,  $\beta=1.53$ , and  $\gamma=1.57$ . E. Posnjak and H. E. Merwin gave for the artificial crystals:

	F-	Tl-	Na-	C-	Li-light
$\alpha$ . . .	1.542	1.536	1.531	1.527	1.526
$\beta$ . . .	1.559	1.552	1.546	1.541	1.540
$\gamma$ . . .	1.620	1.600	1.597	1.589	1.587

D. Mawson observed that the mineral is readily decomposed by ammonia—liquid, soln., or gas.

According to A. Maus, if a conc. soln. of ferric sulphate be treated with calcium hydroxide or carbonate until the precipitate no longer dissolves, and the liquid be rapidly filtered, the dark brown filtrate contains **ferric oxydisulphate**, with  $\text{Fe}_2\text{O}_3:\text{SO}_3=1:2$ . The salt is also formed by agitating a conc. soln. of ferric sulphate with the precipitate obtained by treating an excess of ferric sulphate with ammonia in the cold. The yellow deposit formed on crystals of ferrous sulphate on exposure to air also consists of this disulphate, so that a soln. of the altered ferrous sulphate deposits the disulphate when heated. On evaporating the soln. of the disulphate, a gummy yellowish-brown mass is formed; and when the soln. is allowed to stand for some time, disulphate is precipitated whilst the normal sulphate remains in soln. This decomposition is less complete the more conc. the soln.; and for complete decomposition, the soln. must be boiled. The disulphate forms ammonium and potassium salts; and it expels the normal sulphate from its combination with the alkali sulphates. F. Wibel described a sulphur-yellow, crystalline precipitate, corresponding with  $\text{Fe}_2\text{O}_3.2\text{SO}_3.2\text{H}_2\text{O}$ , said to be formed

by heating a soln. of copper and ferrous sulphates in a closed vessel. The evidence is here too indefinite to establish the existence of these products as chemical individuals.

M. P. Applebey and S. H. Wilkes supposed that an anhydrous basic salt,  $7\text{Fe}_2\text{O}_3 \cdot 15\text{SO}_3$ , or  $5(\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3) \cdot 2\text{Fe}_2\text{O}_3$ , separates at  $25^\circ$  from soln. with between 27 and 30 per cent.  $\text{SO}_3$ . The compound is not formed at  $18^\circ$ , and when the acidity is less than 27 per cent.  $\text{SO}_3$  at  $25^\circ$ , or 29.6 per cent. at  $18^\circ$ , the solid phases are solid soln. of variable composition. According to G. Keppeler and J. d'Ans, if ferrous sulphate be heated in dry air at about  $300^\circ$ , a chocolate-brown powder is formed of sp. gr. 3.83, and in composition it approximates to anhydrous ferric oxy-sulphate. H. O. Hofman and W. Wanjukoff also observed that the oxydisulphate begins to form at  $167^\circ$  when heptahydrated ferrous sulphate is heated in air; and the reaction is completed at  $455^\circ$ ; at a higher temp.,  $492^\circ$  to  $560^\circ$ , it begins to form red ferric oxide. The compound was similarly made by E. Kothny.

E. Posnjak and H. E. Merwin prepared the *monohydrate* of ferric oxydisulphate,  $\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot \text{H}_2\text{O}$ , may be  $\text{Fe}(\text{OH})\text{SO}_4$ , under the conditions indicated in Figs. 661 to 668. It is formed above  $75^\circ$  in the system  $\text{Fe}_2\text{O}_3$ - $\text{SO}_3$ - $\text{H}_2\text{O}$ , when the percentage proportions of these three components are 14.31 to 19.74:22.71 to 30.80:62.98 to 49.46 at  $110^\circ$ ; 12.05 to 15.35:22.39 to 30.88:65.66 to 53.77 at  $140^\circ$ ; and 0.63 to 1.91:5.58 to 48.94:93.79 to 49.15 at  $200^\circ$ . The crystals are very pale orange-yellow, with pleochroism  $\alpha$  and  $\beta$  colourless, and  $\gamma$  clear yellow. The rhombic crystals appear as fibrous crusts, and rough prisms. The indices of refraction are:

	F-	Tl-	Na-	C-	Li-light
$\alpha$ . . .	1.814	1.796	1.783	1.772	1.770
$\beta$ . . .	1.844	1.821	1.804	1.790	1.788
$\gamma$ . . .	1.968	1.940	1.918	1.897	1.894

L. Darapsky described a red mineral from Rio Loa, Chili, and he called it **rubrite**—in allusion to its red colour. When an allowance is made for the gypsum and epsomite present as impurities, its composition corresponds with the *trihydrate* of ferric oxydisulphate,  $\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot 3\text{H}_2\text{O}$ , or  $\text{Fe}(\text{OH})\text{SO}_4 \cdot \text{H}_2\text{O}$ . No place has been found for the trihydrate on the equilibrium diagrams, Figs. 661 to 668. C. Lausen found deep orange-yellow crystals of what he called **butlerite**—after G. M. Butler—as a product of the burning of pyrite ore in a mine at Jerome, Arizona. Analyses correspond with the *pentahydrate* of ferric oxydisulphate,  $\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot 5\text{H}_2\text{O}$ , or  $\text{Fe}(\text{OH})\text{SO}_4 \cdot 2\text{H}_2\text{O}$ . E. Posnjak and H. E. Merwin prepared the pentahydrate under the conditions indicated in Figs. 661 to 668. The salt is stable below  $100^\circ$ , and, taking percentage proportions of  $\text{Fe}_2\text{O}_3$ : $\text{SO}_3$ : $\text{H}_2\text{O}$ , the salt is stable at  $75^\circ$  when these are 17.78 to 20.93:23.10 to 30.11:59.12 to 48.96; and at  $50^\circ$ , when they are 17.96 to 21.0:22.96 to 28.2:59.08 to 50.8. The monoclinic crystals have the axial ratios  $a:b:c=0.858:1:1.358$ , and  $\beta=71^\circ 24'$ . C. Lausen said that the crystals of butlerite are rhombic with the axial ratios  $a:b:c=0.9005:1:1.3606$ . The crystals were said to be optically negative, and to have a moderately high birefringence. E. Posnjak and H. E. Merwin said that the diamond-shaped, microscopic, monoclinic crystals have a transverse zone of twinning, with twinning planes normal to the symmetry plane. The basal cleavage is good; and C. Lausen said that one direction of the cleavage parallel to the  $b$  pinacoid is good, but the other direction of the cleavage, also pinacoidal, is imperfect. Butlerite is slightly pleochroic, being pale brownish-yellow in the  $\alpha$ -direction, and pale canary-yellow in the  $\gamma$ -direction. E. Posnjak and H. E. Merwin said that  $\alpha$  is colourless;  $\beta$ , faint yellow; and  $\gamma$ , light yellow. C. Lausen found the sp. gr. of butlerite to be 2.548; the hardness 2.5; and the indices of refraction  $\alpha=1.604$ ,  $\beta=1.674$ , and  $\gamma=1.731$ . E. Posnjak and H. E. Merwin gave for the indices of refraction of the pentahydrate:

	F-	Tl-	Na-	C-	Li-light
$\alpha$ . . .	1.603	1.594	1.588	1.581	1.580
$\beta$ . . .	1.702	1.688	1.678	1.669	1.667
$\gamma$ . . .	1.782	1.765	1.749	1.735	1.733

A. Frenzel described a mineral from Carracoles, Chili, which he called **amarantite**—from the flower amaranth—in allusion to its colour; a slightly altered form was called **hohmannite**—after T. Hohmann; and a variety from Sierra Gorda was called **paposite**, by L. Darapsky. A. Frenzel, however, showed that paposite, hohmannite, and amarantite belong to the same mineral species. Analyses reported by L. Darapsky, A. Frenzel, J. B. Macintosh, R. Scharizer, F. A. Genth, and M. Gräbner correspond with the *heptahydrate* of ferric oxydisulphate,  $\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot 7\text{H}_2\text{O}$ . E. A. Wülfing found that no water is lost when amarantite is heated between  $40^\circ$  and  $50^\circ$ ; and R. Scharizer observed a loss of 11.29 per cent. when amarantite is confined over conc. sulphuric acid, and when heated to:

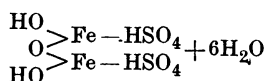
	$75^\circ$	$100^\circ$	$150^\circ$	$200^\circ$	$250^\circ$	$300^\circ$	$>300^\circ$
Loss . . .	11.61	12.30	17.82	23.46	25.76	26.91	28.22 per cent.

The dehydration curve from R. Scharizer's data shows two breaks approximately at  $100^\circ$  and at  $200^\circ$  corresponding with losses of 3 and 6 mols. respectively. A. Frenzel, F. A. Genth, and L. Darapsky found that 12.3 per cent., or 3 mols. of water are lost at  $100^\circ$ . R. Scharizer accordingly represented the formula of the heptahydrate,  $\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot 7\text{H}_2\text{O}$ , by  $(\text{HO} \cdot \text{Fe})_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , or  $\text{HO} \cdot \text{Fe} : \text{SO}_4 \cdot 3\text{H}_2\text{O}$ . Amarantite is orange-yellow at  $150^\circ$ , and brownish-red at  $200^\circ$ . Amarantite usually occurs in columnar, bladed, or radiating masses, or in slender prismatic crystals with the (100)- and (010)-faces vertically striated. The colour is orange-red, brownish-red, or amaranth-red. The pleochroism on  $\alpha$  is stronger than on  $\beta$ , which is brownish-red or lemon-yellow. The streak is lemon-yellow. The optical measurements of S. L. Penfield, in agreement with those of E. A. Wülfing, show that the triclinic crystals have the axial ratios  $a : b : c = 0.76915 : 1 : 0.57383$ , and  $\alpha = 95^\circ 38' 15''$ ,  $\beta = 90^\circ 23' 32''$ , and  $\gamma = 97^\circ 13' 4''$ . The (100)-, and (010)-cleavages are perfect. The optical character is negative; and the optic axial angles  $2E = 59^\circ 3'$  for Li-light, and  $2E = 63^\circ 3'$  for Na-light. The sp. gr. is 2.11, according to A. Frenzel, whilst S. L. Penfield gave 2.286; the hardness is 2.5.

L. Darapsky described a chestnut-brown mineral from Sierra Gorda, Chili, which he called **castanite**—from *castanea*, a chestnut, in allusion to the colour. A. F. Rogers described specimens from Knoxville, California. According to L. Darapsky, and A. F. Rogers, the analysis corresponds with the *octohydrate*,  $\text{Fe}_2\text{S}_2\text{O}_9 \cdot 8\text{H}_2\text{O}$ . The mineral occurs in prismatic crystals more or less dull and rounded, and united in massive aggregates, or in minute crystals lining cavities. The crystals are monoclinic with a prismatic angle of  $82^\circ$ . According to A. F. Rogers, the prismatic crystals are triclinic with the axial ratios  $a : b : c = 0.726 : 1 : 0.895$ , and  $\alpha = 89^\circ 50'$ ,  $\beta = 91^\circ 10'$ , and  $\gamma = 78^\circ 46'$ . The cleavage parallel to (010) is perfect, and those parallel to (110) and to  $(\bar{1}\bar{1}0)$  are less well developed. According to L. Darapsky, the streak is orange-yellow; the sp. gr. 2.118; and the hardness, 3. A. F. Rogers gave 2.2 for the sp. gr., and he found that the indices of refraction are  $\alpha = 1.553$ ,  $\beta = 1.643$ , and  $\gamma = 1.657$ , and  $\gamma - \alpha = 0.104$ . M. C. Bandy gave the hardness 2.5, and  $\alpha = 1.550$ ,  $\beta = 1.645$ , and  $\gamma = 1.660$ . According to L. Darapsky, when castanite is heated, it loses water:

	$50^\circ$	$80^\circ$	$100^\circ$	$145^\circ$	$170^\circ$	$>170^\circ$
Loss . . .	1.0	9.5	11.8	15.5	20.5	10.2 per cent.

The general behaviour thus resembles that of amarantite, but the loss with amarantite over  $200^\circ$  is 1 mol., and with castanite, 2 mols. A. F. Rogers reported a break in the dehydration curve at  $27^\circ$ . The constitutional formula given by R. Scharizer is:



Castanite is only slightly soluble in water; but it dissolves in warm hydrochloric acid, but in the cold the attack is slow. It remains unchanged in air, and in a desiccator over calcium chloride. A specimen exposed to sunlight crumbled to powder.

H. Rose described a pale yellow or white mineral from Tierra Amarilla, Chili, and a similar mineral has been reported from Paillières, Dept. du Gard; Cetine, Tuscany; Cape Calamita, Elba; and from Red Cliff, California. It was called **fibroferrite** by J. Prideaux; *stypcticite*, by J. F. L. Hausmann; and *copiapite*, by J. L. Smith. Analyses by J. L. Smith, T. L. Walker, E. Tobler, F. Field, A. Brun, G. Linck, L. Darapsky, F. Pisani, I. Domeyko, R. Scharizer, E. Manasse, R. A. A. Johnston, H. Rose, and J. Prideaux correspond generally with the *decahydrate*,  $\text{Fe}_2\text{S}_2\text{O}_9 \cdot 10\text{H}_2\text{O}$ , although in some cases  $11\text{H}_2\text{O}$  is nearer the mark. R. Scharizer found the loss on heating to be:

	50°	60°	70°	85°	100°	160°	175°	192°	>192°
Loss . . .	12.17	15.00	19.38	24.40	25.63	28.00	33.01	33.19	36.93

Observations were made by G. Linck, and E. Manasse. The results are taken to correspond with the formula:  $(\text{HO} \cdot \text{Fe})_2(\text{SO}_4)_2 \cdot 9\text{H}_2\text{O}$ , i.e.  $\text{HO} \cdot \text{Fe} : \text{SO}_4 \cdot 4\frac{1}{2}\text{H}_2\text{O}$ , or  $\text{HO} \cdot \text{Fe} : \text{SO}_4 \cdot 5\text{H}_2\text{O}$ . Fibroferrite occurs in delicately fibrous aggregates thought by G. Linck to be monoclinic. The pleochroism is marked— $\alpha$  and  $\beta$  are colourless, and  $\gamma$  is amber-yellow. The optical character is positive. E. Manasse gave for the indices of refraction  $\alpha=1.568$ , and  $\gamma=1.530$ ; E. S. Larsen,  $\alpha=1.525$  to  $1.533$ ,  $\beta=1.534$ , and  $\gamma=1.565$  to  $1.575$ ; and T. L. Walker,  $\alpha=1.518$ ,  $\beta=1.518$ , and  $\gamma=1.561$ . J. L. Smith gave 1.84 for the sp. gr.; and G. Linck, 1.857. The hardness is 2.0 to 2.5.

H. Moissan mentioned the *dodecahydrate*,  $2\text{Fe}_2\text{O}_3 \cdot 5\text{SO}_3 \cdot 12\text{H}_2\text{O}$ , as occurring in nature in the form of the mineral mysite. O. Meister observed that an iron-pickling acid deposited hyacinth-red, monoclinic crystals of the *pentadecahydrate* of ferric oxydisulphate,  $\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot 15\text{H}_2\text{O}$ . The crystals effloresce in air; when heated, they melt in their water of crystallization, and lose 35 to 36 per cent. of water; they are sparingly soluble in water; and are decomposed by water, especially if heated.

A. Breithaupt described a mineral from the tin-mines of Ehrenfriedersdorf, and Bolivia, which he called **raimondite**—after A. Raimondi. The analysis corresponds with the empirical formula:  $2\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 7\text{H}_2\text{O}$ , or **ferric trioxyltrisulphate**. M. Berthelot obtained anhydrous  $2\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3$  by calcining the sulphate. G. C. Wittstein, and F. Muck reported an octohydrate to be formed by oxidizing a soln. of ferrous sulphate in air. A. Mailhe also obtained a hydrate  $2\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot n\text{H}_2\text{O}$  by the prolonged action of mercuric oxide on a soln. of ferrous sulphate. The *heptahydrate* raimondite occurs in thin, six-sided tables with replaced basal edges, and also in scale-like crystals which are hexagonal or trigonal. The colour is honey-yellow or ochre-yellow. The basal cleavage is perfect. A. des Cloizeaux said that the crystals are uniaxial and the optical character is negative. E. S. Larsen gave  $\omega=1.82$  to  $1.867$ , and  $\epsilon=1.79$ . W. T. Schaller, and E. S. Larsen regard raimondite to be really jarosite. A. Meillet found yellow, friable nodules in the clay beds of Meudon, and Auteuil. The analysis corresponded very nearly with the *hemihydrate*,  $2\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ , and he called it **apatelite**. W. T. Schaller regards apatelite as one with jarosite. J. D. Dana found that the mineral named **pastreite**—after M. Pastré—by L. Bergemann is related to raimondite; and W. T. Schaller, J. D. Dana, and L. Azéma suggested that pastreite was impure jarosite. Pastreite occurs in yellow, amorphous, reniform masses at Paillières, Dept. du Gard. L. Darapsky described a mineral from Paposa, Atacama, and he called it **paposite**. The dark red mineral occurs in crystals, and in fibrous radiating masses. The analysis approximates  $2\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 10\text{H}_2\text{O}$ .

N. Athanasesco heated a 25 per cent. soln. of ferric sulphate at  $150^\circ$  and obtained pale yellow rhombohedra of **ferric pentoxyltritetrasulphate**,  $3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$ ;



if a 3 per cent. soln. be used, the product approximates  $10\text{Fe}_2\text{O}_3 \cdot \text{SO}_3 \cdot \text{H}_2\text{O}$ , and it was thought to be a mixture. E. Posnjak and H. E. Merwin also obtained the *enneahydrate* with the same composition under the conditions indicated in Figs. 661 to 668; it is stable in contact with soln. up to about  $170^\circ$ . The salt was found to be stable with the proportions by weight,  $\text{Fe}_2\text{O}_3 : \text{SO}_3 : \text{H}_2\text{O} = 1.44$  to  $17.96 : 2.30$  to  $22.96$ ;  $96.26$  to  $59.08$  at  $50^\circ$ ;  $0.93$  to  $17.98 : 1.62$  to  $23.10 : 97.45$  to  $59.12$  at  $75^\circ$ ;  $0.08$  to  $14.31 : 0.83$  to  $22.71 : 99.09$  to  $62.96$  at  $110^\circ$ ; and  $0.8$  to  $11.5 : 3.5$  to  $19.0 : 95.7$  to  $69.5$  at  $140^\circ$ . It is readily obtained above  $75^\circ$ . G. Tunell and E. Posnjak studied the X-radiograms. E. Posnjak and H. E. Merwin found that the orange-yellow, rhombohedral crystals have the axial ratio  $a : c = 1 : 1.14$ , and they appear in rhombs with deep bases; and the rhombs are nearly cubes. The pleochroism  $\omega$  is deep yellow, and  $\epsilon$  light yellow. The powder appears orange-yellow. The indices of refraction are:

	F-	Tl-	Na-	C-	Li-light
$\omega$ . . .	1.865	1.836	1.816	1.799	1.797
$\epsilon$ . . .	1.755	1.739	1.728	1.728	1.716

M. Saxén reported a yellow, earthy product of the weathering of the pyrites at Otravaara, Finland, and he named it **borgströmite**—after J. L. H. Borgström. The analysis approximates  $\text{Fe}_2\text{O}_3 \cdot \text{SO}_3 \cdot 3\text{H}_2\text{O}$ , but later observations indicate that its formula is more likely to be **ferric pentoxytetrasulphate**,  $3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$ , and this is in agreement with the observations of E. Posnjak and H. E. Merwin.

A. Breithaupt described a mineral occurring in the fissures in mica-slate in Labrador; J. D. Dana, and F. Pisani said Greenland. It also occurs at St. Léger, near Mâcon, Chihuahua, Mexico, and was called **carphosiderite**—from *κάρφος*, straw; and *σίδηρος*, iron. Analyses reported by E. Wittich, A. Lacroix, and F. Pisani approximate the *decahydrate*,  $3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 10\text{H}_2\text{O}$ . W. T. Schaller represents it by a formula of the utahite type,  $[\text{Fe}(\text{OH})_2]_2\text{SO}_4$ , namely,  $\text{H}_2[\text{Fe}(\text{OH})_2]_6(\text{SO}_4)_4$ —*vide infra*, jarosite. The colour is pale yellow, or deep straw; and the streak is yellowish. The mineral occurs in reniform masses and incrustations, and also in lamellæ. The crystals are uniaxial and possibly rhombohedral; the cleavage is basal; the optical character is positive; and the birefringence is strong. A. Breithaupt gave 2.49 to 2.50 for the sp. gr., and F. Pisani, 2.728. The hardness is 4.0 to 4.5.

E. Soubeiran added potassium carbonate to a soln. of ferric sulphate so long as the alkali does not produce a permanent turbidity, and heated the red liquid until a precipitate is formed. The light reddish-yellow powder had a composition corresponding with the *trihydrate* of **ferric dioxysulphate**,  $\text{Fe}_2\text{O}_3 \cdot \text{SO}_3 \cdot 3\text{H}_2\text{O}$ . A. Arzruni described an orange-yellow incrustation on the quartz in the Tintic district, Utah, and he called the mineral **utahite**. Analyses by A. Damour, and K. Thaddeëff approximate to the *dihydrate*,  $\text{Fe}_2\text{O}_3 \cdot \text{SO}_3 \cdot 2\text{H}_2\text{O}$ . The constitutional formula may be, as suggested by K. Thaddeëff,  $[(\text{HO})_2\text{Fe}-\text{SO}_4-\text{Fe}(\text{OH})_2]$ ; R. Scharizer gave  $[\text{Fe}(\text{OH})_2]_6[\text{SO}_4]_3$ ; and S. L. Penfield,  $[(\text{HO})_2\text{Fe}]_8[\text{SO}_4]_{14}$ . Utahite occurs in aggregates of fine scales consisting of tabular hexagonal crystals with rhombohedral faces. A. Arzruni gave for the axial ratio of the rhombohedral crystals  $a : c = 1 : 1.0576$ . The optical character is negative, and the crystals are often optically anomalous. The pleochroism is strong—pale yellow and yellowish-brown. The index of refraction given by E. S. Larsen is  $\omega = 1.82$ . W. T. Schaller considered utahite to be the same mineral species as jarosite. The mineral is said to be insoluble in water and nitric acid.

L. Darapsky reported a mineral in the Lautaro mine, Morro Moreno, Atacama, which he called **planoferrite**. Analyses correspond with the *pentadecahydrate*,  $\text{Fe}_2\text{O}_3 \cdot \text{SO}_3 \cdot 15\text{H}_2\text{O}$ . The mineral was also described by F. Grünling. The colour is yellowish-green to brown, and the streak is chrome-yellow. The hexagonal plates are probably rhombic, and they have a basal cleavage, and faces on the edges. The hardness is 3.

P. F. Reinsch described sulphur-yellow, soft, chalk-like aggregates of microscopic crystals found in the dolerite of Chrysophone, Cyprus; and he called it *cyprusite*. According to H. Fulton, the analysis approximates  $\text{Al}_2(\text{SO}_4)_3 \cdot 8\text{Fe}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ , when deductions are made for impurities. R. Scharizer added that the formula may be that of the *hexahydrate*,  $\text{R}_2\text{O}_3 \cdot \text{SO}_3 \cdot 6\text{H}_2\text{O}$ . The six-sided plates are probably hexagonal; and the optical character is negative. E. S. Larsen gave for the indices of refraction  $\omega = 1.803$  and  $\epsilon = 1.72$ . W. T. Schaller regarded *cyprusite*, as well as *utahite*, *carphosiderite*, *apatelite*, *raimondite*, and *pastreite* as crystallographically equivalent to *jarosite*.

According to J. J. Berzelius, if a soln. of ferric sulphate be treated with insufficient ammonia for complete decomposition, or if an aq. soln. of ferrous sulphate is exposed to the air, **ferric pentoxysulphate**,  $2\text{Fe}_2\text{O}_3 \cdot \text{SO}_3 \cdot 6\text{H}_2\text{O}$ , is formed. It is also deposited in vitriol and alum works by the action of air on the mother-liquors. C. Weltzien said that the same compound is formed when a soln. of ferrous sulphate is treated with hydrogen dioxide. The analyses of G. C. Wittstein, and F. Muck show that the composition of the precipitate varies with the conditions. S. U. Pickering regarded  $2\text{Fe}_2\text{O}_3 \cdot \text{SO}_3 \cdot n\text{H}_2\text{O}$ , or, as he wrote it,  $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{Fe}_2\text{O}_3$ , as the only basic salt capable of existence as a chemical individual. W. N. Rae also found that the white precipitate deposited on keeping soln. of ammonium ferric alum, has the composition  $2\text{Fe}_2\text{O}_3 \cdot \text{SO}_3 \cdot n\text{H}_2\text{O}$ . C. Weltzien represented it as the *octohydrate*; O. Meister, as the *heptahydrate*; and J. J. Berzelius, and F. Muck as the hexahydrate, which they obtained by oxidizing a soln. of ferrous sulphate with hydrogen dioxide. F. Cornu believed that *glockerite*,  $2\text{Fe}_2\text{O}_3 \cdot \text{SO}_3 \cdot 6\text{H}_2\text{O}$ , is an adsorption compound of hydrated ferric oxide.

J. J. Berzelius said that the *hexahydrate* occurs in nature in the form of what he called *Vitriolocker*, or *vitriol ochre*, which F. S. Beudant called *pittizite*—a name applied to a hydrated ferric sulphatoarsenate. C. F. Naumann employed the term **glockerite**—after E. F. Glocker. Analyses, reported by J. J. Berzelius, F. Hochstetter, L. A. Jordan, T. Scheerer, J. Eyerma, A. H. Church, and J. Thiel, agree with the hexahydrate formula. Vitriol ochre is coloured brown to ochre-yellow, dull green, and brownish-black to pitch-black; and it may be earthy, massive, or stalactitic. A. Breithaupt and O. L. Erdmann also described a vitriol ochre from the alum-shale quarry at Grunsdorf which had a sp. gr. 1.8, and was rather more hydrated than *glockerite*; and E. Greenly called a similar specimen, an *octohydrate*,  $2\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot 8\text{H}_2\text{O}$ , from Parys Mountain, Anglesey, **hydroglockerite**.

Other products have been analyzed. T. Scheerer found that that obtained by boiling a dil. soln. of ferric sulphate approximates  $3\text{Fe}_2\text{O}_3 \cdot \text{SO}_3 \cdot 4\text{H}_2\text{O}$ ; E. F. Anthon, by precipitating a soln. of ferric sulphate with barium acetate, and adding baryta-water to the filtrate, obtained  $4\text{Fe}_2\text{O}_3 \cdot \text{SO}_3 \cdot n\text{H}_2\text{O}$ ; and T. Scheerer, obtained a product corresponding with  $7\text{Fe}_2\text{O}_3 \cdot \text{SO}_3 \cdot 10.5\text{H}_2\text{O}$  or  $6\text{Fe}_2\text{O}_3 \cdot \text{SO}_3 \cdot 10\text{H}_2\text{O}$ , by the weathering of iron pyrites in alum shale. N. Athanasesco obtained what he regarded as  $10\text{Fe}_2\text{O}_3 \cdot \text{SO}_3 \cdot \text{H}_2\text{O}$ , by heating a 3 to 4 per cent. soln. of ferric sulphate in a sealed tube at  $275^\circ$ . The crystals of the dark brown powder are not well-defined.

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#### § 47. Complex Salts with Ferric Sulphate

M. Lachaud and C. Lepière<sup>1</sup> prepared ammonium ferric trisulphate,  $3(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3$ , or  $(\text{NH}_4)_3\text{Fe}(\text{SO}_4)_3$ , by dissolving ferrous or ferrous ammonium sulphate in a fused ammonium sulphate, washing out the excess of ammonium sulphate from the cold mass with alcohol, and again heating the product with ammonium sulphate. The white, prismatic needles have a sp. gr. of 2.31 at 14°. If the heating be prolonged, ammonium ferric disulphate,  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3$ , or  $\text{NH}_4\text{Fe}(\text{SO}_4)_2$ , crystallizing in hexagons, is formed. R. F. Weinland and F. Ensgraber obtained a similar salt, as a white crystalline powder, by heating a soln. of ammonium ferric alum with sulphuric acid for some hours. M. Lachaud and C. Lepière found that the sp. gr. is 2.45 at 14°; and O. Pettersson gave 2.54 at 16.8°. The salt is sparingly soluble in water. R. F. Weinland and F. Ensgraber regard it as a salt of ferridisulphuric

acid,  $\text{H}[\text{Fe}(\text{SO}_4)_2]$ . J. J. Berzelius, G. Forchhammer, and E. Mitscherlich obtained crystals of the *dodecahydrate*, or *ammonium ferric alum*,  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ , by crystallization from a mixed soln. of the component salts. If the crystals have a yellow tinge, this is due to the presence of an excess of the ferric salt and it disappears when the salt is re-crystallized. M. L. Negri and A. A. Bado described manufacturing this alum on a large scale for the purification of water. J. L. Howe and E. A. O'Neal obtained the salt by the electrolysis of a soln. of ammonium and ferrous sulphates acidified with sulphuric acid; the cathode is a platinum wire dipping in an acidified soln. of ferrous sulphate contained in a porous pot which is placed in the soln. of mixed sulphates. A current of 0.04 amp. is passed through the cell, and in a few hours, crystals of the alum are deposited round the anode.

The crystals are colourless octahedra and cubo-octahedra belonging to the cubic system, and they are isomorphous with the other members of the alum family. They were studied by Z. Weyberg. According to J. Bonnell and E. P. Perman, the violet colour is not due to the presence of a manganese salt as suggested by W. Ostwald, but the pure salt is violet, and the colourless salt is due to the masking of the violet by the complementary yellowish-brown of colloidal ferric hydroxide. L. Vegard and E. Esp examined the X-radiograms, and it was inferred that there are six atoms of oxygen from the water next to the univalent metal, then the sulphate group with a base of the tetrahedron towards the water group, and the point directed towards the trivalent metal. The whole forms a compact unit along the trigonal axis, which is terminated at each end by a metallic atom. L. Vegard and A. Maurstad found the X-radiogram of the anhydrous salt,  $\text{NH}_4\text{Fe}(\text{SO}_4)_2$ , corresponded with a hexagonal space-lattice having  $a=4.825 \text{ \AA}$ , and  $c=8.310 \text{ \AA}$ , and a mol. of the salt per unit cell. According to A. Knop, when the crystals are placed in the corresponding aluminium salt, they are transformed into pseudomorphs of the latter salt. F. Klocke found crystals optically anomalous. H. Kopp gave 1.712 for the sp. gr.; L. Playfair and J. P. Joule, 1.718; H. Topsøe and C. Christiansen, 1.719; H. G. F. Schröder, 1.700; O. Pettersson, 1.725 at  $17^\circ$  and 1.723 at  $18^\circ$ ; and C. Sorét, 1.713. K. Wendekamm gave for the different iron alums:

	K	Rb	Cs	Tl	$\text{NH}_4$
Specific gravity . . .	1.831	1.952	2.066	2.351	1.719
Mol. volume . . .	274.9	281.6	289.7	284.4	280.5
Index of refraction . .	1.4817	1.4823	1.4838	1.5237	1.4848
Mol. refraction . . .	78.31	80.32	82.81	87.00	80.34

G. T. Gerlach gave for the sp. gr. of aq. soln. at  $15^\circ$ :

$\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	5	10	15	20	25	30	35	40 per cent.
Specific gravity . . .	1.023	1.047	1.071	1.096	1.122	1.148	1.175	1.20

The 20 per cent. soln. is saturated at this temp. W. N. Rae found the sp. gr. of soln. with 0.0080, 0.0502, 0.1000, and 0.2000 grm. of the hydrate per c.c. to be respectively 0.99849, 1.01670, 1.03801, and 1.0796 at  $32.5^\circ$ , and the corresponding mol. soln. vol. are: 99, 113.7, 116.8, and 124.3. According to W. N. Rae, soln. containing C grms. of hydrated alum per c.c. had the sp. gr.:

C . . .	0.2000	0.15000	0.1000	0.0502	0.0350	0.0250	0.0201	0.0080
Sp. gr. . .	1.07960	1.05907	1.03801	1.01670	1.01025	1.00592	1.00376	0.99849

E. Wiedemann studied the changes in vol. which occur when the salt is heated. J. Locke observed that the salt melts in its water of crystallization at  $40^\circ$ . S. Lupton found that the crystals of  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$  lose 23 mols. of water at  $150^\circ$ , and all is lost at  $230^\circ$ . C. Montemartini and E. Vernazza studied the action of heat on the soln. H. C. Jones and E. Mackay measured the lowering of the f.p. of aq. soln., and the results show that the alum exists in the more conc. soln., but in dil. soln. the complex alum molecule is broken down into the simple sulphates which are, in turn, more or less ionized. P. A. Favre and C. A. Valson found the

heat of soln. of a mol of the dodecahydrate in 500 mols of water is  $-16.6$  Cals. According to C. Soret, the indices of refraction,  $\mu$ , are :

	A-	B-	C-	D-	E-	b-	F-	G-
$\mu$ . . .	1.47927	1.48029	1.48150	1.48482	1.48921	1.48993	1.49286	1.49980

whilst H. Topsøe and C. Christiansen gave for the *C*-, *D*-, and *F*- lines, respectively 1.4821, 1.4854, and 1.4934—*vide supra*. T. Swensson studied the action of light and observed no photoelectric effect. H. Kauffmann studied the Faraday effect. J. Errera and H. Brasseur studied the sp. induction and the water of crystallization of the alums.

G. Forchhammer observed that 1 part of the salt dissolves in 3 parts of water ; and J. Locke, that 100 c.c. of water at  $25^\circ$  dissolve 44.15 grms. of the anhydrous salt, or 124.4 grms. of the hydrated salt, so that 1.659 mols of the anhydrous salt can dissolve in a litre of water. Aq. soln. of the salt become turbid when diluted, although conc. soln. will remain clear for months. W. N. Rae found that the addition of ammonium sulphate favours the hydrolysis, whilst sulphuric acid acts in the converse way. The hydrolysis is symbolized :  $2\text{Fe}_2(\text{SO}_4)_3 + 2(\text{NH}_4)_2\text{SO}_4 + 5\text{H}_2\text{O} \rightleftharpoons 2\text{Fe}_2\text{O}_3.\text{SO}_3 + 5\text{H}_2\text{SO}_4 + 2(\text{NH}_4)_2\text{SO}_4$  ; or  $4\text{Fe}^{+++} + \text{SO}_4^{--} + 5\text{H}_2\text{O} \rightleftharpoons 2\text{Fe}_2\text{O}_3.\text{SO}_3 + 10\text{H}^+$ . W. N. Rae found that the change of colour of the soln. which occurs on hydrolysis corresponds with the assumption that the colour is due to the presence of the soluble basic sulphate  $2\text{Fe}_2\text{O}_3.\text{SO}_3$ . W. N. Rae found the precipitate which separates on keeping the aq. soln. is  $\text{Fe}_2\text{O}_3.\text{SO}_3$  ; the colour of the aq. soln. is in agreement with the assumption that a basic soluble salt is present. The white precipitate produced on adding conc. sulphuric acid to the soln. is the anhydrous alum. H. C. Jones and E. Mackay found that the lowering of the f.p. for 0.257*N*-, 0.064*N*-, and 0.0014*N*-soln. were respectively  $1.820^\circ$ ,  $0.505^\circ$ , and  $0.066^\circ$  ; and that the mol. electrical conductivity of soln. with a mol of the salt in *v* litres of water at  $25^\circ$  was :

<i>v</i> . . . . .	4	20	40	200
$\mu$ . . . . .	118.9	177.4	211.5	320.2

C. L. Wagner found that the soln. become turbid, deposit a precipitate, and become colourless without the conductivity becoming constant, or attaining, in the case of the corresponding potassium ferric alum, the value required for soln. of sulphuric acid and potassium sulphate containing the eq. of the  $\text{SO}_4$ -ions. Thus, for soln. with an eq. of ammonium iron alum in *v* litres, time *t* min., the eq. conductivity,  $\lambda$ , was :

<i>t</i> . . . . .	1	2	80	195*	1225	2568	7202 mins.
$\lambda(v=40)$ . . . . .	86.6	86.6	87.1	87.4	95.8	101.6	107.2

Turbidity begins to develop at the time denoted by the asterisk :

<i>t</i> . . . . .	1	2	92	1360*	2875	4350	5995 mins.
$\lambda(v=1600)$ . . . . .	249.0	257.9	295.2	302.2	303.5	304.0	305.1

H. C. Jones and E. Mackay found the electrical conductivity of the soln. increased with time. The values of  $\mu$  for soln. with  $v=200$  increased from 320.2 to 330.0 in 2 hrs. ; and for a soln. with  $v=2000$ , the values of  $\mu$  were 694.0, 808.2, 891.0, and 896.0 respectively in 0, 0.5, 1.8, and 21 hrs. D. E. Olshevsky studied the orientation of the crystals in a magnetic field. J. Forrest found indications of anisotropy, and of magnetic cubic symmetry with the crystals in magnetic fields of the order of 20,000 gauss. The subject was studied by C. G. Montgomerie. C. L. Wagner assumed that the enormous surface of the dispersed colloid adsorbs the acid ions, and that as coagulation proceeds, and the surface is accordingly diminished, the adsorbed acid returns to the soln.

G. Foex, J. Aharoni and F. Simon, and L. C. Jackson examined the magnetic properties of ammonium ferric sulphate. L. A. Welo's results for the

solid and fused salt are summarized in Fig. 580. T. Ishiwara, and K. Honda and T. Ishiwara gave for  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3$ :

	-177.0	-86.6°	22.4°	132.7°	279.7°	409.6°
$\chi \times 10^6$	170.3	91.6	59.6	37.5	50.0	41.9

and for  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ :

	-172.6°	-76.0°	19.0°	129.0°	236.7°	549.2°	931.1°
$\chi \times 10^6$	94.6	46.9	30.6	22.4	18.1	10.8	3.0

H. K. Onnes and E. Oosterhuis found that at  $T^\circ \text{K.}$ , the mass susceptibility  $\chi \times 10^6$ , and the product  $T\chi \times 10^5$ , are:

$T$	200°	169.6°	77.3°	64.6°	20.4°	17.9°	14.7° K.
$\chi \times 10^6$	30.4	51.8	114.7	137	432	492	598
$T\chi \times 10^5$	882	879	887	885	881	881	879

As indicated above, when sulphuric acid is added to a soln. of ammonium ferric alum, a white precipitate approximating  $\text{NH}_4\text{Fe}(\text{SO}_4)_2$  is formed. S. F. Ravitz and R. G. Dickinson studied the photochemical reduction of the salt in the presence of polyiodides; W. Moldenhauer, and E. Mischke, the action of hydrogen sulphide on the salt; M. N. Mittra and N. R. Dhar, the catalytic action of the salt on the oxidation of sulphurous acid; N. Schiloff and B. Nebrassoff, the adsorption of the salt by *schönite*. A. Purgotti represented the reaction with hydrazine by the equation:  $5\text{N}_2\text{H}_4 + 4\text{Fe}_2\text{O}_3 = 8\text{FeO} + 4\text{NH}_3 + 3\text{N}_2 + 4\text{H}_2\text{O}$ ; and M. Bobtelsky and D. Kaplan, the effect of this salt on the decolorization of soln. of potassium permanganate. L. R. W. McCay and W. T. Anderson studied the reducing action of mercury, which is rapid and complete at  $60^\circ$  to  $70^\circ$ ; and Y. Ono, the action of ammonium oxalate.

According to A. Maus, when ammonia is added to a soln. of ammonium ferric alum until the precipitate is no longer dissolved, and the dark brown liquid is allowed to evaporate spontaneously, short, regular, six-sided prisms of the basic salt **ammonium ferric oxytetrasulphate**,  $2(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}_2\text{O}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ , are formed. One part of the salt is soluble in 2.4 parts of water. J. C. G. de Marignac added that the salt loses half its water in vacuo at ordinary temp., or in air at  $100^\circ$ . Ammonia is evolved at a higher temp. D. E. Olshevsky studied the orientation of the crystals in a magnetic field.

A. Grimm and G. Ramdohr obtained **potassium ferric heptasulphate**,  $\text{K}_2\text{SO}_4 \cdot 2\text{Fe}_2(\text{SO}_4)_3$ , in white, tabular crystals, as a by-product in the preparation of carbon monoxide from a soln. of 1 part of potassium ferrocyanide and 9 parts of conc. sulphuric acid. A. Étard prepared **potassium ferric trisulphate**,  $3\text{K}_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3$ , or  $\text{K}_3\text{Fe}(\text{SO}_4)_3$ , as a white powder insoluble in water, but slowly decomposed by that liquid. R. F. Weinland and F. Ensgraber obtained **potassium ferric disulphate**,  $\text{K}_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3$ , or  $\text{K}[\text{Fe}(\text{SO}_4)_2]$ , by heating a soln. of potassium ferric alum for some hours with sulphuric acid. The *dodecahydrate*,  $\text{KFe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , or *potassium ferric alum*,  $\text{K}_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ , is formed by allowing a mixture of conc. soln. of potassium and ferric sulphates to stand for some days at  $0^\circ$ . The salt was so prepared by R. Richter, and W. Heintz. The electrolytic process employed for the ammonium salt is not good because of the low solubility of potassium sulphate. W. Heintz noted that the commercial salt is usually contaminated with potassium sulphate. The crystals of potassium ferric alum are octahedra, isomorphous with the other members of the family of alums. R. Hollemann studied this subject. G. Tammann and A. Sworykin studied the solid soln. with potassium alum. W. Richter observed that the crystals become matte on exposure to air. C. Christiansen showed that the purified salt furnishes colourless crystals, and that the violet colour is due to the presence of some manganese alum. H. Topsøe and C. Christiansen gave 1.831 for the sp. gr.; O. Pettersson, 1.819 to 1.831; and C. Soret, 1.806. F. Ephraim and P. Wagner

discussed the mol. vol.—*vide suprah.* G. T. Gerlach gave for the sp. gr. of aq. soln. at 15° :

KFe(SO <sub>4</sub> ) <sub>2</sub> .12H <sub>2</sub> O	5	10	15	20	25	30	35 %
Specific gravity	1.025 (1.0268)	1.0507 (1.0466)	1.0773 (1.0672)	1.1050 (1.0894)	1.1340 (1.1136)	1.1645 (1.1422)	1.1967 (1.1967)

The values in brackets were determined by B. Franz at 17.5°. J. Beckenkamp found that the elastic modulus perpendicular to the (110)-face is 1862 kgms. per sq. mm. J. Locke observed that the salt melts in its water of crystallization at 28°. R. Scharizer observed that the loss of water at different temp. is as follows :

Loss	48° 30.59	60° 36.02	70° 40.10	87° 40.35	100° 41.24	114° 41.41	152° 43.03 per cent.
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showing that of the 42.93 per cent. of water contained by potassium ferric alum, K<sub>2</sub>SO<sub>4</sub>.Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>.24H<sub>2</sub>O, about 40 per cent.—corresponding with 22 mols.—is given off below 70°, and that the last 2 mols. are given off slowly as the temp. rises to 152°. These two mols. of water are supposed to represent constitutional water, the other 22 mols., water of crystallization. W. Richter found that at a red-heat it is decomposed into ferric oxide and potassium sulphate, and sulphur trioxide ; whilst W. Heintz observed that at a lower temp.—between 60° and 100°—the reaction can be symbolized : 10KFe(SO<sub>4</sub>)<sub>2</sub>=2Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>+5(K<sub>2</sub>O.3Fe<sub>2</sub>O<sub>3</sub>.12SO<sub>3</sub>).+2SO<sub>3</sub>. C. Montemartini and E. Vernazza studied the action of heat on the soln. S. Miyamoto studied the reduction of the salt in hydrogen in the electric discharge. E. F. Anthon showed that 1 part of the salt dissolves in 5 parts of water at 12.5°. The salt is insoluble in alcohol. The soln. of potassium ferric alum in a little hot water was observed by W. Richter to deposit a greenish-yellow salt which is afterwards converted into the alum and redissolved. The brown colour of the aq. soln. was attributed by H. Rose to the presence of a basic salt in soln. ; the soln. in dil. sulphuric acid is colourless—*vide supra*, ammonium ferric alum. The hydrolysis of aq. soln. was studied by C. R. C. Tichborne. R. Scharizer showed that potassium ferric alum cannot be re-crystallized from its aq. soln. at room temp. because hydrolysis occurs, metavoltine (*q.v.*) is precipitated, and the soln. becomes more acid. K. Someya studied the reduction of the salt with lead amalgam.

According to W. F. Foshag, the *dihydrate*, K<sub>2</sub>SO<sub>4</sub>.Fe(SO<sub>4</sub>)<sub>3</sub>.2H<sub>2</sub>O, occurs as a mineral at Borate, San Bernardino Co., California, and he called it **krausite**—after E. H. Kraus. It occurs in aggregates of crystals with a pale mauve colour superposed on the yellow colour of the purer mineral. The prismatic crystals are monoclinic with the axial ratios *a* : *b* : *c*=1.5401 : 1 : 1.7584, and β=102° 44'. The basal cleavage is good, and that parallel to the (100)-face is also good. The sp. gr. is 2.840, and the hardness 2.5. The crystals are biaxial, the optical character is positive ; the optic axial angle is very large ; the indices of refraction are α=1.588, β=1.650, and γ=1.722 ; and the birefringence is large. Krausite is insoluble in water ; and is slowly hydrolyzed when left in contact with water. It dissolves slowly and completely in hydrochloric acid.

R. Scharizer observed that when an aq. soln. of potassium ferric alum is allowed to crystallize, metavoltine—*vide infra*—is precipitated, and the soln. becomes acidic ; but if the soln. be evaporated to dryness the metavoltine disappears, and a pale violet salt takes its place. The same salt is obtained when a soln. of the composition of the alum is acidified with sulphuric acid and allowed to crystallize. An analysis of the salt corresponds with K<sub>2</sub>Fe<sub>2</sub>S<sub>4</sub>O<sub>16</sub>.8H<sub>2</sub>O, or the *tetrahydrate*, KFeS<sub>2</sub>O<sub>8</sub>.4H<sub>2</sub>O. The losses which occur when the salt is heated to different temp. are :

Loss	48° 3.31	57° 4.41	70° 0.04	72° 13.25	114° 19.32	152° 19.64 per cent.
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The dehydration curve, Fig. 672, shows thin breaks corresponding with the loss of 3, 6, and 7 mols. of water. This is taken to mean that 2 of the 8 mols. of water are constitutional, so that the formula is H<sub>2</sub>K<sub>2</sub>[Fe(OH)]<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>.6H<sub>2</sub>O, or more simply, **potassium ferric dihydrodisulphate**,



E. Beutel and A. Kutzelnigg found that exposure to ultra-violet light hastens the dehydration of the salt.

The monoclinic crystals have the axial angles  $a : b : c = 0.95016 : 1 : 1.0221$ , and  $\beta = 72^\circ 43'$ . The birefringence is large. The sp. gr. is 2.403. Small crystals are white, but in masses, the colour appears reddish-violet. The salt is readily soluble in water, for 100 parts of water at ordinary temp. dissolve 22 parts of the salt. The salt in dil. soln. is hydrolyzed, and the insoluble end-product of the hydrolysis corresponds with  $\text{K}_2\text{Fe}_2\text{S}_4\text{O}_{25}$ .

E. Soubeiran added potassium carbonate to a soln. of ferric sulphate until the precipitate no longer redissolved, and mixed the dark brown liquid with alcohol in excess. The light reddish-brown precipitate, after washing with alcohol, corresponded with  $2\text{K}_2\text{SO}_4 \cdot 3\text{Fe}_2\text{O}(\text{SO}_4)_2 \cdot 22\text{H}_2\text{O}$ . The moist precipitate is soluble in water, but not if it has been dried. The salt is decomposed by water. T. Scheerer triturated potassium iron alum with absolute alcohol, and obtained a yellow powder,  $4\text{K}_2\text{O} \cdot 3\text{Fe}_2\text{O}_3 \cdot 12\text{SO}_3 \cdot 24\text{H}_2\text{O}$ ; by similarly treating a conc., aq. soln. of the alum with absolute alcohol, the brownish-green precipitate, after drying 13 days at  $18^\circ$ , had the composition:  $8\text{K}_2\text{O} \cdot 6\text{Fe}_2\text{O}_3 \cdot 24\text{SO}_3 \cdot 39\text{H}_2\text{O}$ , and if the precipitate be dried over sulphuric acid in vacuo, he said that the composition is:  $3\text{K}_2\text{O} \cdot 2\text{Fe}_2\text{O}_3 \cdot 8\text{SO}_3 \cdot 9\text{H}_2\text{O}$ ; but if the precipitate when formed be boiled for 1 minute, the composition is  $5\text{K}_2\text{O} \cdot 3\text{Fe}_2\text{O}_3 \cdot 12\text{SO}_3 \cdot 12\text{H}_2\text{O}$ . There is little doubt that these products represent mixtures produced by the hydrolysis of potassium iron alum.

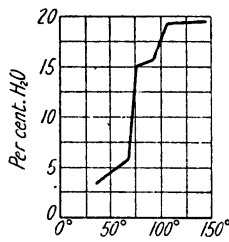


FIG. 672.—Dehydration Curve of  $\text{K}_2\text{Fe}_2\text{S}_4\text{O}_{16} \cdot 8\text{H}_2\text{O}$ .

A. Maus observed that if potassium hydroxide be added to a soln. of potassium ferric alum until the precipitate no longer dissolves, and the dark brown liquid be allowed to evaporate spontaneously, yellowish-brown, regular, six-sided prisms shortened into plates are deposited. A similar salt was prepared by E. F. Anthon from a soln. of 78 parts of ferric oxide, 147 parts sulphuric acid, and 87.2 parts of potassium sulphate; and by W. Richter, by adding a boiling soln. of potassium sulphate to a supersaturated soln. of ferric sulphate. R. Scharizer also observed that this salt is formed by the action of a soln. of potassium hydrosulphate on hydrated ferric oxide. The analyses discussed by A. Maus, T. Scheerer, C. F. Rammelsberg, E. F. Anthon, W. Richter, and J. C. G. de Marignac correspond approximately with **potassium ferric dioxydodecasulphate**,  $5\text{K}_2\text{O} \cdot 3\text{Fe}_2\text{O}_3 \cdot 12\text{SO}_3 \cdot 18\text{H}_2\text{O}$ , or  $5\text{K}_2\text{SO}_4 \cdot 2\text{Fe}(\text{SO}_4)_3 \cdot \text{Fe}_2\text{O}_2(\text{SO}_4) \cdot 18\text{H}_2\text{O}$ . This compound is sometimes called *Maus' salt*—W. Haidinger called it *mausite*. The crystals were examined by J. C. G. de Marignac, and W. Haidinger noted that they are optically anomalous like tourmaline. A. Maus found that 1 part of the salt dissolves in 6 parts of cold water, and the aq. soln. soon deposits crystals of basic ferric sulphate. E. F. Anthon said that if the salt be treated with hot water there remains a pale yellow powder with the composition:  $\text{K}_2\text{O} \cdot 3\text{Fe}_2\text{O}_3 \cdot 10\text{SO}_3 \cdot 18\text{H}_2\text{O}$ . T. Scheerer said that if this salt be kept for a long time in a warm, dry place, the efflorescence has the composition:  $10\text{K}_2\text{O} \cdot 6\text{Fe}_2\text{O}_3 \cdot 24\text{SO}_3 \cdot 33\text{H}_2\text{O}$ .

J. Blaas obtained from the pyritiferous trachytes of Madeni Zakh, Persia, yellow aggregates of minute six-sided plates, which he called **metavoltine**. F. Zambonini found the mineral in the Grotta di Zolfo, Miseno and Vesuvius; E. Aguilar, at the solfatara of Pozzuoli, Naples; and A. Lacroix, in a fumarole near Pyromeni, Island of Milo, and near Porto di Levante, Vulcano. Analyses reported by J. Blaas, F. Zambonini, and R. Scharizer correspond with the formula  $5(\text{K}_2, \text{Na}_2, \text{Fe})\text{O} \cdot 3\text{Fe}_2\text{O}_3 \cdot 12\text{SO}_3 \cdot 18\text{H}_2\text{O}$ , or, in the idealized case,  $\text{K}_{10}\text{Fe}_6\text{S}_{12}\text{O}_{50} \cdot 18(\text{or } 19)\text{H}_2\text{O}$ . R. Scharizer found that the dehydration curves—averaged for  $\alpha$ -metavoltine in Fig. 673—correspond with losses of the order:

	34°	48°	75°	100°	134°	145°	154°	184°	243°
Loss . . .	4.15	5.77	6.35	7.44	10.13	11.71	13.04	14.05	14.71 per cent.

There are breaks at about  $60^\circ$ ,  $120^\circ$ , and  $130^\circ$ , corresponding respectively with the



decahydrate, the pentahydrate, and the trihydrate. It is therefore supposed that four mols. of water are constitutional, and that the formula for metavoltine is:  $\text{H}_2\text{K}_{10}[\text{Fe}(\text{OH})_6](\text{SO}_4)_{12} \cdot 14$  (or 15)  $\text{H}_2\text{O}$ . There are differences in the reported proportions of water of crystallization. R. Scharizer observed that when the crystals are left exposed to air, they crumble to powder. The original crystals correspond with  $\text{H}_2\text{K}_{10}[\text{Fe}(\text{OH})_6](\text{SO}_4)_{12} \cdot 15\text{H}_2\text{O}$ , and those which have crumbled to powder have only  $12\text{H}_2\text{O}$ , and are pseudomorphous with the original hexagonal crystals. B. Gössner and M. Arm gave  $\text{K}_2\text{H}_7(\text{SO}_4)_6 \cdot 3\text{Fe}(\text{OH})_3 \cdot \text{H}_2\text{O}$  for the formula.

R. Scharizer observed that there are two forms of this salt, both of which have the formula:  $\text{H}_2\text{K}_{10}[\text{Fe}(\text{OH})_6](\text{SO}_4)_{12} \cdot 15\text{H}_2\text{O}$ . The ordinary form, called  $\alpha$ -metavoltine, has hexagonal crystals, is optically negative, and has a sp. gr. of 2.403; the other form, called  $\beta$ -metavoltine, has triclinic crystals, is optically negative, and has a sp. gr. 2.339. Hexagonal  $\alpha$ -metavoltine crystallizes easily from soln. of potassium and ferric sulphates containing an excess of one of these salts. The amount of potassium sulphate in excess is without influence, but with ferric sulphate certain limits must not be exceeded—*vide infra*, the hydrolysis of metavoltine. If the soln. of the two sulphates, acidified with sulphuric acid, be treated with alcohol, and the orange-red, gelatinous mass be left in contact with the mother-liquor for 24 hrs., crystals of  $\alpha$ -metavoltine are formed. The exact conditions for the formation of  $\beta$ -metavoltine have not been determined, but a high concentration of substances which hinder the hydrolysis of the  $\alpha$ -salt is necessary, and in some cases both the  $\alpha$ - and  $\beta$ -salts crystallize from the same soln. The soln. of the  $\alpha$ -salt is transformed into the  $\beta$ -salt when the liquid is mixed with substances which impart an acidity to the soln.—*e.g.*, sulphuric acid, potassium hydrosulphate, or rhomboclase—but not normal potassium sulphate. The transformation can be recognized as the green soln. becomes brown. B. Gössner and M. Arm prepared metavoltine by keeping a soln. of 300 grms. of water, 19.5 grms. potassium sulphate, and 27 grms. of ferric sulphate in a round flask on a sand-bath at  $70^\circ$  to  $80^\circ$  for some days. Metavoltine is obtained by evaporating the soln. at ordinary temp., but the product appears in the form of crystalline crusts.

B. Gössner and M. Arm found that nearly half the water of crystallization is lost at ordinary temp. in a short time. According to R. Scharizer, the dehydration curves of  $\alpha$ - and  $\beta$ -metavoltine, Fig. 673, are similar, but the  $\beta$ -salt is rather more stable when heated in air. R. Scharizer also found that 100 parts of water at ordinary temp. dissolve 11.52 parts of  $\alpha$ -metavoltine and 4.68 parts of potassium hydrosulphate, or else 7.04 parts of  $\beta$ -metavoltine and 4.62 parts of potassium hydrosulphate. Hence the  $\beta$ -salt appears to be the stable form, and the  $\alpha$ -salt the labile form of metavoltine.

B. Gössner and M. Arm found that the hexagonal prisms have the axial ratio  $a : c = 1 : 0.957$ ; and that the X-radiograms correspond with a unit cell containing 8 mols., and with the parameters  $A = 19.43 \text{ \AA}$ ., and  $c = 18.60 \text{ \AA}$ . J. Blaas gave 2.53 for the sp. gr. of metavoltine; and B. Gössner and M. Arm gave 2.396; and found the mol. wt. to be 117.5. J. Blaas gave 2.5 for the hardness. The hexagonal, yellow crystals are pleochroic,  $\omega$  is yellow to chestnut-brown, and  $\epsilon$ , pale yellow or green. E. S. Larsen found the indices of refraction to be  $\omega = 1.588$ , and  $\epsilon = 1.578$ . Unlike copiapite, metavoltine is sparingly soluble in water. J. Blaas said that metavoltine dissolves slowly in hydrochloric acid, and slowly and imperfectly in cold water. The aq. soln. deposits a red powder when it is heated. R. Scharizer said that the aq. soln. of metavoltine is at first undecomposed, but hydrolysis sooner or later occurs according to the concentration. The metavoltine splits into potassium sulphate and an unstable residue,  $\text{Fe}_6\text{S}_7\text{O}_{30}$ , or  $2\text{Fe}_2(\text{SO}_4)_3 \cdot \text{Fe}_2\text{O}_2(\text{SO}_4)$ , then decomposes until the soluble part approximates to  $\text{Fe}_2(\text{SO}_4)_3$ , and utahite,  $\text{Fe}_2\text{O}_2\text{SO}_4$ , is precipitated. The ferric sulphate is hydrolyzed liberating sulphuric

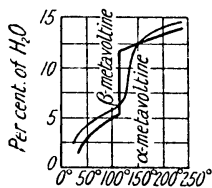


FIG. 673.—Dehydration Curves of Metavoltine.



W. F. Hillebrand and S. L. Penfield consider that the jarosites are solfataric products having been formed under the combined action of heat and press. Their sparing solubility explains how they occur as fine crystalline powders like many precipitates. A. Mitscherlich obtained jarosite by heating a mixture of ferric and potassium sulphates in a sealed tube at  $260^{\circ}$ .

Jarosite is coloured ochre-yellow, yellowish-brown, or clove-brown. It occurs in minute, indistinct crystals in druses, and less frequently in rhombohedral crystals somewhat resembling cubes with tetrahedral planes. The mineral also occurs in fibrous, or compact masses, and in nodules or incrustations with a tuberoso or coral-loidal surface. The rhombohedral crystals were found by G. A. König to have the axial ratio  $a : c = 1 : 1.2492$ ; and W. F. Hillebrand and S. L. Penfield gave  $1 : 1.245$  for jarosite;  $1 : 1.216$  for plumbojarosite; and  $1 : 1.104$  for natrojarosite. G. Cesaro's value,  $1 : 1.1689$ , probably referred to a mixed jarosite. The crystals were also studied by A. Breithaupt, and N. von Kokscharoff. W. F. Hillebrand and F. E. Wright found a specimen of plumbojarosite which was pleochroic,  $c$  being dark brownish-red, and  $a$  pale golden-yellow. The (0001)-cleavage is distinct. According to J. G. Fairchild, the crystals are uniaxial and optically negative, with the indices of refraction  $\epsilon = 1.71$  and  $\omega = 1.80$ . E. S. Larsen gave  $\omega = 1.82$ .

According to W. F. Hillebrand and S. L. Penfield, the jarosite family may be taken to include the alunites so as to furnish the isomorphous series :

Alunite . . . . .	$K_2[Al(OH)_2]_6(SO_4)_4$
Natroalunite . . . . .	$Na_2[Al(OH)_2]_6(SO_4)_4$
Jarosite . . . . .	$K_2[Fe(OH)_2]_6(SO_4)_4$
Ammoniojarosite . . . . .	$(NH_4)_2[Fe(OH)_2]_6(SO_4)_4$
Natrojarosite . . . . .	$Na_2[Fe(OH)_2]_6(SO_4)_4$
Argentojarosite . . . . .	$Ag_2[Fe(OH)_2]_6(SO_4)_4$
Plumbojarosite . . . . .	$Pb[Fe(OH)_2]_6(SO_4)_4$
Carphosiderite . . . . .	$H_2[Fe(OH)_2]_6(SO_4)_4$

Carphosiderite was added to the series by W. T. Schaller. W. F. Hillebrand and S. L. Penfield continued : Assuming that these represent the mol. formulæ, there are in each molecule fifty atoms, to one Pb-atom or one group  $K_2$  or  $Na_2$ . Hence, these fifty atoms, by virtue of their mass effect, dominate the situation, and an isomorphism between such unlike elements as potassium, sodium, and lead is not so surprising as might at first appear. Although the  $K_2$ ,  $Na_2$ , and Pb units play so small a part in these molecules, the substitution of  $Na_2$  for  $K_2$  is attended by a marked variation in the angles of the crystals, greater, in fact, than is generally observed in isomorphous replacements. The likeness between alunite and jarosite would be anticipated from the closeness of the axial ratios of corundum,  $Al_2O_3$ , and hæmatite,  $Fe_2O_3$ , since the ratios  $a : c$ , for the two minerals, are respectively  $1 : 3630$ , and  $1 : 3656$ . The lengths of the  $c$ -axis in these minerals are :

Alunite	Jarosite	Natrojarosite	Plumbojarosite
1.252	1.245	1.104	1.216

so that the substitution of sodium for potassium in jarosite produces a greater variation than the substitution of Pb for  $K_2$ . The optical character of the jarosites is positive; that of alunite is negative. E. S. Larsen gave for the indices of refraction of natrojarosite,  $\omega = 1.832$ , and  $\epsilon = 1.750$ , or  $\omega - \epsilon = 0.082$ , and for plumbojarosite,  $\omega = 1.875$ , and  $\epsilon = 1.784$ , or  $\omega - \epsilon = 0.091$ . W. F. Hillebrand and F. E. Wright gave for plumbojarosite,  $\omega = 1.825$ , and  $\epsilon = 1.785$ , and said that the crystals in convergent polarized light are uniaxial, optically negative and with a strong birefringence. The sp. gr. of jarosite is  $3.15$  to  $3.26$ ; and the hardness  $2.5$  to  $3.5$ . D. Mawson observed that the mineral is readily decomposed by ammonia—liquid, soln., or gas.

R. Scharizer prepared **potassium ferric trisulphate**,  $K_6Fe_2(SO_4)_6 \cdot nH_2O$ , or  $Fe(KSO_4)_3 \cdot nH_2O$ , analogous to ferrinatriite (*q.v.*), and he accordingly named it **ferrikalite**.

H. Erdmann, C. Soret, M. le Blanc and P. Rohland prepared **rubidium ferric disulphate**,  $RbFe(SO_4)_2 \cdot 12H_2O$ , or **rubidium ferric alum**,  $Rb_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 24H_2O$ ,

from a soln. of the constituent salts, and J. L. Howe and E. A. O'Neal, by the electrolytic method employed for the ammonium salt. The octahedral crystals are colourless or a delicate violet; they are isomorphous with the members of the alum family. C. Soret gave 1.916 for the sp. gr.; and M. le Blanc and P. Rohland gave 1.952 for the solid, and 1.0381 and 1.0575 respectively for soln. with 7.11 and 10.55 per cent. of the salt—*vide supra*. J. Locke found that the salt melts in its water of crystallization at 53°. H. Erdmann said 33°. C. Soret found for the index of refraction,  $\mu$ :

	A-	B-	C-	D-	E-	b-	F-	G-light
$\mu$	1.47700	1.47770	1.47894	1.48234	1.48654	1.48712	1.49003	1.49700

M. le Blanc and P. Rohland gave  $\mu=1.4823$  for the solid with Na-light; and 1.3395 and 1.3427 respectively for soln. with 7.11 and 10.55 per cent. of salt. The corresponding sp. and mol. refractions with the  $\mu$ -formula are 0.2501 and 36.36 and with the  $\mu^2$ -formula, 0.1489 and 20.46 for the soln. with 7.11 per cent. of salt; and for soln. with 10.55 per cent. of salt, and the  $\mu$ -formula respectively 0.2488 and 34.19, and with the  $\mu^2$ -formula, 0.1485 and 20.40. The crystals acquire a green tinge on exposure to air. J. Locke found the solubilities in water at 25° and 30° to be respectively 97.4 and 202.4 grms.  $\text{Rb.Fe}(\text{SO}_4)_2$  per litre; at 35° and 40°, the soln. decomposes precipitating a basic salt.

C. Soret prepared **caesium ferric disulphate**,  $\text{CsFe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , or *caesium ferric alum*,  $\text{Cs}_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ , from a soln. of the component salts; and J. L. Howe and E. A. O'Neal, by the electrolytic process used for the ammonium salt. The octahedral crystals are colourless or a delicate violet, and the crystals acquire a green tinge on exposure to air. They are isomorphous with the members of the alum family. C. Soret gave 2.061 for the sp. gr.—*vide supra*. J. Locke found that the salt melts in its water of crystallization at 71°. C. Soret gave for the index of refraction,  $\mu$ :

	A-	B-	C-	D-	E-	b-	F-	G-light
$\mu$	1.47825	1.47921	1.48042	1.48378	1.48797	1.48867	1.49136	1.49838

J. Locke found the solubilities of the salt in water at 25°, 30°, 35°, and 40° to be respectively 17.1, 25.2, 37.5, and 60.4 grms. of  $\text{CsFe}(\text{SO}_4)_2$  per litre.

A. Raimondi, and I. Domeyko described a lemon-yellow or orange-yellow mineral occurring in the San Simon mine, Huantajaya, Chili, and it was called **sideronatrite**. Analyses reported by A. Raimondi, A. Frenzel, and F. A. Genth correspond with  $2\text{Na}_2\text{O} \cdot \text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 7\text{H}_2\text{O}$ . F. A. Genth observed that about 4 mols. of water are lost at 110°, and A. Frenzel, that all is lost at 300°. R. Scharizer found that sideronatrite with 14.63 per cent. of water loses 9.43 per cent. of water in a desiccator; while at 100° it loses 10.30 per cent.; at 125°, 4.13 per cent.; at 165°, 0.15 per cent., and at 205°, 0.05 per cent. This means that 6 mols. of water are lost at 125°, and the remaining mol. at higher temp. Allowing for the mol. of constitutional water, the formula can be written:  $[\text{NaSO}_4]_4[\text{Fe}(\text{HO})]_2 \cdot 6\text{H}_2\text{O}$ , or **sodium ferric hydrodisulphate**,  $(\text{NaSO}_4)_2\text{Fe}(\text{OH}) \cdot 3\text{H}_2\text{O}$ , analogous with potassium ferric dihydrosulphate. A. Skrabal synthesized the mineral by heating a soln. of 50 grms. of ferric sulphate and 10 c.c. of dil. sulphuric acid (1 : 6) with 300 grms. of hydrated sodium sulphate on a water-bath. R. Scharizer crystallized soln. of ferric sulphate, or acid sulphate and sodium sulphate, and obtained sideronatrite so long as the proportion of sulphuric acid in the soln. is not too great, and the proportion of  $\text{Na}_2\text{O} : \text{Fe}_2\text{O}_3$  is less than about 2, otherwise ferrinatrite is formed.

Sideronatrite occurs in orange-yellow or straw-yellow, crystalline masses of fine, fibrous structure which separate into thin splinters. S. L. Penfield found that the crystals are rhombic; A. Raimondi said monoclinic; and A. Frenzel, triclinic. The cleavage is probably pinacoidal. The optical character is positive. Pleochroism is not very marked—F. A. Genth said that *a* and *b* are colourless, and *c* is straw-yellow, and E. S. Larsen, that *a* is colourless, *b* is pale amber-yellow, and *c* is amber-yellow. The optic axial angle  $\alpha V=58^\circ 5'$ ; and the indices of

refraction  $\alpha=1.508$ ,  $\beta=1.525$ , and  $\gamma=1.586$ . The sp. gr. given by F. A. Genth is 2.153, and by S. L. Penfield, 2.355; the hardness is 2.0 to 2.5. The mineral is virtually insoluble in cold water, but is decomposed by boiling water with the separation of hydrated ferric oxide. It is soluble in acids.

A. Frenzel described a lemon-yellow or orange-yellow mineral which he called *urusite*, obtained from the Urus plateau, on the naphtha island Cheleken, in the Caspian Sea. It occurs in pulverulent earthy forms, and also in lumps consisting of minute, rhombic crystals. The composition is very close to that of sideronatrite, being  $2\text{Na}_2\text{O} \cdot \text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 8\text{H}_2\text{O}$ , so that J. D. Dana considered both to be the same mineral species. The sp. gr. is 2.22. P. T. Cleve described an impure sideronatrite obtained from St. Bartholomew, West Indies, and he called it *bartholomite*. Its composition, allowing for impurities, is  $2\text{N}_2\text{O} \cdot \text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 3\text{H}_2\text{O}$ .

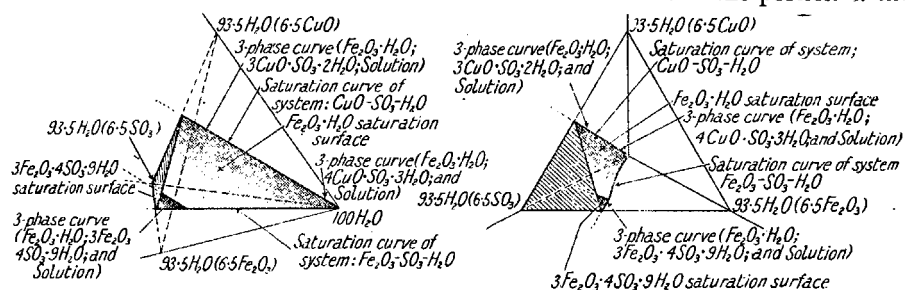
J. B. Macintosh described a mineral from Sierra Gorda, Chili, which he called *ferrinatrite*, but since the contained iron is ferric, not ferrous, R. Scharizer altered it to **ferrinatrite**. A. Frenzel called the mineral *gordaitite*. Analyses reported by J. B. Macintosh, F. A. Genth, and A. Frenzel agree with the formula:  $3\text{Na}_2\text{O} \cdot \text{Fe}_2\text{O}_3 \cdot 6\text{SO}_3 \cdot 6\text{H}_2\text{O}$ . F. A. Genth said 3 mols. of water are lost at  $100^\circ$ , and J. B. Macintosh 5.5 mols.; and R. Scharizer observed that nearly all the water is lost at  $100^\circ$ , so that none is considered to be constitutional water, and he wrote the formula:  $\text{Fe}_2(\text{NaSO}_4)_6 \cdot 6\text{H}_2\text{O}$ , or **sodium ferric trisulphate**,  $\text{Fe}(\text{NaSO}_4)_3 \cdot 3\text{H}_2\text{O}$ . R. F. Weinland and F. Ensgraber wrote the formula:  $\text{Na}_3[\text{Fe}(\text{SO}_4)_3] \cdot 3\text{H}_2\text{O}$ . A. Skrabal prepared this salt by melting sodium sulphate in its water of crystallization, and adding ferric sulphate and conc. sulphuric acid. R. F. Weinland and F. Ensgraber prepared the salt by mixing a soln. of 0.01 mol of ferric sulphate in 50 c.c. of water, with 0.03 to 0.05 mol of sodium sulphate in 50 c.c. of water, and 0.08 mol of sulphuric acid; heating the mixture on a water-bath until half the water had evaporated; and allowing the mixture to cool slowly for 24 hrs. R. Scharizer obtained it by allowing a mixture of ferric and sodium acid sulphates to stand for some time in moist air; and also by employing the method used for the preparation of sideronatrite but using soln. strongly acidified with sulphuric acid. R. Scharizer observed that if ferrinatrite be allowed to stand in moist air for a long time it passes into sideronatrite; and conversely, if sideronatrite be allowed to stand in a conc. sulphuric acid soln., it passes into ferrinatrite.

Ferrinatrite is white, may be pale green or pale grey. It rarely occurs in distinct acicular crystals, more usually in spherical forms with a lamellar and stellate structure. According to A. Arzruni, the rhombohedral crystals have the axial ratio  $a:c=1:0.55278$ . The  $(10\bar{1}0)$ -cleavage is perfect, but the  $(11\bar{2}0)$ -cleavage is not so distinct. The optical character of the uniaxial crystals is positive. S. L. Penfield gave for the indices of refraction for yellow-light,  $\omega=1.558$  and  $\epsilon=1.613$ ; and F. Zambonini,  $\omega=1.5559$  and  $\epsilon=1.627$ . F. A. Genth gave 2.547 to 2.578 for the sp. gr., and 2 for the hardness. Ferrinatrite is soluble in water, and insoluble in alcohol. For **sodium ferric hydroxytetrasulphate**, *vide supra*, natrojarosite. H. Ungemach described **amarillite**,  $\text{NaFe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , in pale yellow, monoclinic crystals from Tierra Amarilla, Chili. The axial ratios are  $a:b:c=0.7757:1:1.1482$ , and  $\beta=84^\circ 33'$ .

R. Jirovsky and F. Ulrich applied the term **slavikite**—after F. Slavik—to small, tabular, rhombohedral crystals with the axial ratio  $a:c=1:1.03$ , found at Valachov, Czechoslovakia. The analysis corresponds with  $(\text{Na},\text{K})_2\text{SO}_4 \cdot \text{Fe}_{10}(\text{HO})_6(\text{SO}_4)_{12} \cdot 63\text{H}_2\text{O}$ . The crystals are pleochroic being greenish-yellow parallel to  $c$ , and colourless perpendicular to  $c$ . The optical character of the uniaxial crystals is negative; and the indices of refraction for sodium light are  $\omega=1.530$ , and  $\epsilon=1.506$ . The sp. gr. is 1.905.

G. Tunell and E. Posnjak studied a portion of the quaternary system:  $\text{CuO}-\text{Fe}_2\text{O}_3-\text{SO}_3-\text{H}_2\text{O}$  in the region involving 93.5 per cent. or more  $\text{H}_2\text{O}$ ; 6.5 per cent. or less of  $\text{Fe}_2\text{O}_3$ ; 6.5 per cent. or less of  $\text{CuO}$ ; and 6.5 per cent. or less of  $\text{SO}_3$  at  $50^\circ$ . The results are summarized in Figs. 674 and 675 on the surfaces of an equilateral tetrahedron. There are five crystalline phases:  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$  (geo-

thite);  $3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$ ;  $\text{CuO}$  (tenorite);  $4\text{CuO} \cdot \text{SO}_3 \cdot 3\text{H}_2\text{O}$  (brochantite); and  $3\text{CuO} \cdot \text{SO}_3 \cdot 2\text{H}_2\text{O}$  (antlerite), in this portion of the system, but no double salt was stable in this region. The  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$  saturation surface in the quaternary system extends from the saturation curve of  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$  in the system,  $\text{Fe}_2\text{O}_3 \cdot \text{SO}_3 \cdot \text{H}_2\text{O}$ , almost to the saturation curves of  $4\text{CuO} \cdot \text{SO}_3 \cdot 3\text{H}_2\text{O}$  and  $3\text{CuO} \cdot \text{SO}_3 \cdot 2\text{H}_2\text{O}$  in the system,  $\text{CuO} \cdot \text{SO}_3 \cdot \text{H}_2\text{O}$ , the three-phase curves,  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ,  $4\text{CuO} \cdot \text{SO}_3 \cdot 3\text{H}_2\text{O}$ , solution, and  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ,  $3\text{CuO} \cdot \text{SO}_3 \cdot 2\text{H}_2\text{O}$ , solution, lying extremely close to the saturation curves of  $4\text{CuO} \cdot \text{SO}_3 \cdot 3\text{H}_2\text{O}$  and  $3\text{CuO} \cdot \text{SO}_3 \cdot 2\text{H}_2\text{O}$  in the system,  $\text{CuO} \cdot \text{SO}_3 \cdot \text{H}_2\text{O}$ . Again, the 3-phase curve:  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ,  $3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$ , solution, extending from the triple point:  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ,  $3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$ , solution, of the system,  $\text{Fe}_2\text{O}_3 \cdot \text{SO}_3 \cdot \text{H}_2\text{O}$ , at successively higher  $\text{CuO}$  percentages intersects planes parallel to the  $\text{Fe}_2\text{O}_3 \cdot \text{CuO} \cdot \text{SO}_3$  face of the co-ordinate tetrahedron in which the percentage of  $\text{H}_2\text{O}$  is successively lower (the planes referred to are those in any one of which the percentage of  $\text{H}_2\text{O}$  is a constant); Fig. 674 is a perspective view of a model of the isothermal-isobaric saturation surface in the portion of the



Figs. 674 and 675.—Portion of the Quaternary System:  $\text{Fe}_2\text{O}_3\text{--CuO--SO}_3\text{--H}_2\text{O}$ , at  $50^\circ$ .

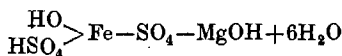
system,  $\text{Fe}_2\text{O}_3\text{--CuO--SO}_3\text{--H}_2\text{O}$ , in which the total composition is 93.5 per cent. or more  $\text{H}_2\text{O}$ , 6.5 per cent. or less  $\text{Fe}_2\text{O}_3$ , 6.5 per cent. or less  $\text{CuO}$ , and 6.5 per cent. or less  $\text{SO}_3$ ; and Fig. 675 is a perspective view of a model of the isothermal-isobaric saturation surface in the portion of the system,  $\text{Fe}_2\text{O}_3\text{--CuO--SO}_3\text{--H}_2\text{O}$ , in which the total composition is 93.5 per cent. or more  $\text{H}_2\text{O}$ , 6.5 per cent. or less  $\text{Fe}_2\text{O}_3$ , 6.5 per cent. or less  $\text{CuO}$ , and 6.5 per cent. or less  $\text{SO}_3$ .

W. Bastick prepared **copper ferric tetrasulphate**,  $\text{Cu}[\text{Fe}(\text{SO}_4)_2]_2 \cdot 24\text{H}_2\text{O}$ , or **copper ferric alum**,  $\text{CuSO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ , from an acid soln. of eq. proportions of the component salts. In addition to the *tetracosihydrate*, C. Lausen observed a *heptahydrate* of copper ferric tetrasulphate,  $\text{CuO} \cdot \text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 7\text{H}_2\text{O}$ , occurring in sky-blue, rhombic crystals, and the mineral was named **ransomite**—after F. L. Ransome. It was formed by the burning of pyritic ore in a mine at Jerome, Arizona. The rhombic crystals have the axial ratios  $a : b : c = 1.7407 : 1 : 0.5168$ . The cleavage—either pinacoidal or prismatic—is perfect. The sp. gr. is 2.632; the hardness is 2.5; the optical character is positive; and the indices of refraction are  $\alpha = 1.631$ ,  $\beta = 1.643$ , and  $\gamma = 1.695$ . The crystals of **guildite** found in the same locality are dark chestnut-brown and monoclinic with the axial ratios  $a : b : c = 1.037 : 1 : 1.407$ , and  $\beta = 74^\circ 43'$ . The composition approximates  $3(\text{Cu}, \text{Fe})\text{O} \cdot 2(\text{Fe}, \text{Al})_2\text{O}_3 \cdot 7\text{SO}_3 \cdot 17\text{H}_2\text{O}$ ; the sp. gr. is 2.725; the hardness is 2.5; the optical character is positive; and the indices of refraction are  $\alpha = 1.623$ ,  $\beta = 1.630$ , and  $\gamma = 1.684$ . For **silver ferric hydrotetrasulphate**,  $\text{Ag}_2\text{O} \cdot 3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot \text{H}_2\text{O}$ , *vide supra*, argentojarosite.

According to Z. Karaoglanoff, barium sulphate can adsorb a little ferric sulphate from aq. soln., and when barium chloride is added to soln. of sulphuric acid or soluble sulphates containing ferric salts, the precipitated barium sulphate is contaminated with iron either adsorbed or in solid soln. G. McP. Smith, however, considers that an insoluble compound—**barium ferric disulphate**,  $\text{Ba}[\text{Fe}(\text{SO}_4)_2]_2 \cdot n\text{H}_2\text{O}$ —is formed.

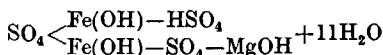
W. Bastick prepared **magnesium ferric tetrasulphate**,  $\text{Mg}[\text{Fe}(\text{SO}_4)_2]_2 \cdot 24\text{H}_2\text{O}$ , or *magnesium ferric alum*,  $\text{MgSO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ , from a soln. of eq. proportions of the component salts acidified with sulphuric acid.

J. J. Berzelius described a *rother Eisenvitriol*, from Falun, Sweden, which was called **botryogen**—from  $\beta\acute{o}\tau\rho\upsilon\varsigma$ , a bunch of grapes, and  $\gamma\epsilon\upsilon\rho\iota\varsigma$ , producing—by W. Haidinger, and *botryite*, or rather *botryte*, by E. F. Glocker; F. S. Beudant called it *neophase*; and A. S. Eakle, *palacheite*—after C. Palache. The mineral also occurs in Madeni Zakh, Persia, at Knoxville, California, and in Peru. Analyses reported by J. G. Gahn and J. J. Berzelius, J. Blaas, R. Mauzelius, P. T. Cleve, J. Hockauf, and A. S. Eakle correspond with  $2\text{MgO} \cdot \text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 15\text{H}_2\text{O}$ . H. Sjögren gave  $\text{Mg}(\text{FeOH})(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$ . A. S. Eakle found that at  $160^\circ$ , four-fifths of the water is given off; R. Scharizer regarded this as water of crystallization, and he wrote the formula:  $(\text{MgOH})_2(\text{FeOH})_2(\text{SO}_4)_2(\text{HSO}_4)_2 \cdot 12\text{H}_2\text{O}$ , or  $\text{H}_2(\text{MgOH})_2(\text{FeOH})_2(\text{SO}_4)_4 \cdot 12\text{H}_2\text{O}$ . The former is analogous to A. Recoura's ferrisulphuric acid, and the constitutional formula represents the salt as **magnesium ferric trihydrodisulphate**:



Botryogen is deep hyacinth-red, or when massive, sometimes ochre-yellow. It usually occurs in reniform or botryoidal shapes or globules with a crystalline surface. It may occur in short, prismatic crystals with the (110)- and (120)-faces vertically striated. The crystals are monoclinic, and  $\beta=62^\circ 26\frac{1}{2}'$ ; A. S. Eakle gave  $0.6554:1:0.3996$ , and  $\beta=117^\circ 9'$ , whilst R. Scharizer, with a different orientation, gave  $1.2245:1:0.8265$ , and  $\beta=99^\circ 35'$ . The (110)-cleavage is distinct; and the (120)-cleavage in traces. The pleochroic-crystals parallel to *c* are orange, and vertical to *c*, orange-grey; E. S. Larsen gave *a* pale yellow, *b* pale red, and *c* orange. The indices of refraction are  $\alpha=1.544$ ,  $\beta=1.548$ , and  $\gamma=1.572$  for sodium light. The optical axial angle  $2V=40^\circ 54'$ . R. Mauzelius gave 2.13 for the sp. gr., and A. S. Eakle, 2.13. The hardness is 2.0 to 2.5. The mineral is stable in a dry atm., but in a moist atm. it becomes covered with a dirty yellowish powder. It is partly soluble in water, leaving an ochreous residue.

A. Frenzel described a reddish-brown mineral from the Salvador mine, Quatena, Chili, which he called **quetenite**. The analysis corresponds with  $\text{MgO} \cdot \text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 13\text{H}_2\text{O}$ , and it can be represented as **magnesium ferric tetrahydrotrisulphate**:



Quetenite occurs in indistinct crystalline masses or in monoclinic or triclinic crystals, with the prismatic cleavage very distinct. The pleochroism has *a* and *b* colourless, and *c* orange-yellow. E. S. Larsen gave for the optic axial angle,  $2V=32^\circ$ , and for the indices of refraction  $\alpha=1.530$ ,  $\beta=1.535$ , and  $\gamma=1.595$ . A. Frenzel gave 2.08 to 2.14 for the sp. gr., and 3 for the hardness. The mineral is decomposed by water with the separation of hydrated ferric oxide.

L. Darapsky described a mineral from Rio Loa, Atacama, which he called **cubeite**. The analysis corresponds with  $3\text{MgO} \cdot 2\text{Fe}_2\text{O}_3 \cdot 7\text{SO}_3 \cdot 3\text{H}_2\text{O}$ , or perhaps better with  $3(\text{Mg,Ca})\text{O} \cdot 2(\text{Fe,Al})_2\text{O}_3 \cdot 7\text{SO}_3 \cdot 3\text{H}_2\text{O}$ . It occurs in red, elongated pyramids either monoclinic or rhombic.

W. Bastick prepared **zinc ferric tetrasulphate**,  $\text{Zn}[\text{Fe}(\text{SO}_4)_2]_2 \cdot 24\text{H}_2\text{O}$ , or *zinc ferric alum*,  $\text{ZnSO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ , by crystallization from a soln. of eq. proportions of the component salts acidified with sulphuric acid. In addition to this *tetracosihydrate*, R. Scharizer prepared the *tetradecahydrate*,  $\text{ZnSO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$ , by allowing a mixture of zinc sulphate and rhomboclase to stand in contact with moist air for several months. R. Scharizer called it **zinc-römerite**—*vide infra*.

A. Étard prepared **aluminium ferric hydrosulphate**,  $\text{Al}_2(\text{SO}_4)_3 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4$ ,

in microscopic hexagonal plates, by heating to 200° a conc. soln. of 2 mols of ferrous sulphate and a mol of aluminium chloride which had been mixed with nitric acid, and a large excess of sulphuric acid. The sandy deposit was separated by decantation, washed with glacial acetic acid, and dried at 120°. When heated to dull redness, sulphuric acid is evolved, and  $\text{Al}_2(\text{SO}_4)_3 \cdot \text{Fe}_2(\text{SO}_4)_3$  remains as a white, crystalline, insoluble powder. F. Wirth and B. Bakke observed that the solubility of either ferric or aluminium sulphate in water at 25° is lowered by the addition of the other salt. At 25°, 100 grms. of the soln. contain :

$\text{Al}_2(\text{SO}_4)_3$ . . .	—	5.200	5.200	6.626	8.810	10.03	(10.23)	(10.70)
$\text{Fe}_2(\text{SO}_4)_3$ . . .	44.97	42.44	38.83	35.82	34.02	32.42	(31.90)	(31.91)

The brackets indicate that both salts are present in the solid phase. The solubility curves—mols of salt per 1000 grms. liquid, Fig. 676—meet when the

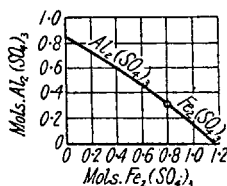


FIG. 676.—Mutual Solubility of Aluminium and Ferric Sulphates.

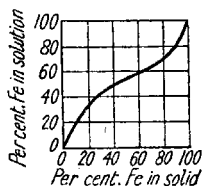


FIG. 677.—Composition of Solution and Solid for Mixtures of Potassium Aluminium and Potassium Ferric Alums.

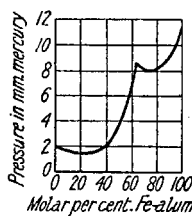


FIG. 678.—Vapour Pressures of Solid Solutions of Potassium Aluminium and Potassium Ferric Alums.

ratio Fe : Al is 1 : 0.3831. There is no evidence of the formation of a compound or solid soln. H. Ungemach described **lapparentite**,  $(\text{Al}, \text{Fe})_2\text{O}_3 \cdot 2\text{SO}_3 \cdot 10\text{H}_2\text{O}$ , from Tierra Amarilla, Chili, with monoclinic crystals having the axial ratios  $a : b : c = 0.2919 : 1 : 0.24155$ , and  $\alpha = 85^\circ 10'$ . R. Holleman found that *potassium aluminium ferric alums* form mixed crystals in all proportions and are isomorphous. Fig. 677 shows the relation between the composition of the soln. and that of the crystals. The vap. press. of the pure salts are respectively 2 mm. and 10.9 mm. There are minima in the vap. press. curve at 1.4 and 7.9 mm., and a maximum at 8.1 mm. when Fe : Al = 2 : 1—Fig. 678. T. Klobb prepared solid soln. of *ammonium aluminium ferric alums*,  $(\text{NH}_4)_2\text{SO}_4 \cdot (\text{Fe}, \text{Al})_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ .

J. E. Willm prepared pale yellow octahedra of **thallous ferric disulphate**,  $\text{TlFe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , or **thallous ferric alum**,  $\text{Tl}_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ , from a soln. of the component salts. C. Soret gave 2.385 for the sp. gr., and O. Pettersson, 2.351. F. Ephraim and P. Wagner discussed the mol. vol.—*vide supra*. J. Locke found that the salt melted at 37° in its water of crystallization. C. Soret found the indices of refraction,  $\mu$ , to be :

	A-	B-	C-	D-	E-	b-	F-	G-light
$\mu$ .	1.51674	1.51790	1.51943	1.52365	1.52859	1.52946	1.53284	1.54112

The salt is not efflorescent, and it is readily soluble in water. J. Locke found that 361.5 grms. of the anhydrous salt or 646 grms. of the hydrate are soluble in a litre of water at 25°; or 0.799 mol of the salt in a litre of water at 25°.

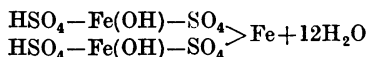
A. Knopf described a hydrated **lead ferric oxytrisulphate**,  $\text{PbO} \cdot 3\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 6\text{H}_2\text{O}$ , differing from *plumbojarosite*,  $\text{PbO} \cdot 3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 6\text{H}_2\text{O}$ ; it was obtained from Clark Co., Nevada, and was called **vegasite**—after Las Vegas, the chief town of the county. It occurs in straw-yellow, ochreous masses consisting of minute fibres and six-sided plates which are optically uniaxial. For *plumbojarosite*, **lead ferric hydroxytetrasulphate**, *vide supra*. B. S. Butler and W. T. Schaller described canary-yellow, earthy, friable masses consisting of microscopic, six-sided



plates, from Beaver Co., Utah; and the mineral was called **beaverite**. It is a **copper lead ferric trioxysulphate**,  $\text{CuO} \cdot \text{PbO} \cdot \text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot 4\text{H}_2\text{O}$ .

A. Étard prepared **chromic ferric hydrosulphate**,  $\text{Cr}_2(\text{SO}_4)_3 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4$ , by the method used for the corresponding aluminium compound. When heated to dull redness it yields the anhydrous salt  $\text{Cr}_2(\text{SO}_4)_3 \cdot \text{Fe}_2(\text{SO}_4)_3$ . T. Klobb prepared solid soln. of *ammonium chromium ferric alums*,  $(\text{NH}_4)_2\text{SO}_4 \cdot (\text{Cr}, \text{Fe})_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ . N. Bjerrum and G. H. Hansen prepared **chromic ferric bromosulphate**,  $[\text{CrBr}_2(\text{H}_2\text{O})_4][\text{Fe}(\text{H}_2\text{O})_6]\text{SO}_4 \cdot 2\text{H}_2\text{O}$ , but not the corresponding chlorosulphate. A. Étard prepared **manganic ferric hydrosulphate**,  $\text{Mn}_2(\text{SO}_4)_3 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4$ , by heating to  $250^\circ$ , the proper proportions of the two sulphates with a mixture of equal vols. of nitric and sulphuric acids added in small quantities at a time. This salt can be converted into  $\text{Mn}_2(\text{SO}_4)_3 \cdot \text{Fe}_2(\text{SO}_4)_3$  by heat. He also prepared **manganous ferric hydrosulphate**,  $2\text{MnSO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 3\text{H}_2\text{SO}_4$ , as well as  $2\text{MnSO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4$ .

J. Sebor described an alum, **ferrous ferric tetrasulphate**,  $\text{Fe}''[\text{Fe}(\text{SO}_4)]_2 \cdot 24\text{H}_2\text{O}$ , or **ferrosic tetrasulphate**, or **ferrous ferric alum**,  $\text{FeSO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ , occurring in white or yellowish-white, radially fibrous masses in the Schwaz lignites near Bilin, Bohemia; and he called the mineral **bilinite**. The sp. gr. of bilinite is 1.875; the hardness, 2; and the index of refraction between 1.495 and 1.501. The double refraction of the acicular crystals is low. In addition to the *tetracosihydrate* just indicated, the *tetradecahydrate* occurs as a mineral which J. Grailich called **römerite**—after A. Römer—and G. Linck called it *bückingite*. It has been found at Goslar, Harz; Rio Tinto, Spain; Madeni Zagh, Persia; and Tierra Amarilla, Chili. Analyses reported by G. Tschermak, R. Scharizer, G. Linck, L. Darapsky, R. E. Landon, H. F. Collins, and J. Blaas, correspond with ferrous ferric tetrasulphate,  $\text{FeO} \cdot \text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 14\text{H}_2\text{O}$ , or better,  $(\text{Fe}, \text{Zn}, \text{Mg})\text{O} \cdot \text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 14\text{H}_2\text{O}$ , or  $\text{FeSO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$ . R. Scharizer found that no water is lost by römerite in a desiccator over conc. sulphuric acid; water begins to come off at about  $70^\circ$ , and the reddish-brown powder then becomes bluish-black. The mineral loses 12 mols. of water below  $130^\circ$ , while very little is lost between  $130^\circ$  and  $250^\circ$ , beyond which temp. the remaining water is expelled. Two mols. of water are accordingly regarded as constitutional, and the formula may be written:



C. A. Anderson observed that the mineral in the United Verde mine, Jerome, Arizona, was probably formed by the action of vapours from burning sulphide ores. R. Scharizer synthesized the mineral by allowing a mixture of powdered ferrous sulphate, and rhomboclase to remain in contact with moist air for several months; it was also prepared from a soln. of the constituent salts in which the concentration exceeds a certain minimum, and in the presence of an excess of sulphuric acid. A soln. with the equivalent of 33.75 per cent. römerite; 8.98 per cent. rhomboclase; 16.46 per cent. sulphuric acid; and 40.81 per cent. of water yields römerite crystals. If the excess of sulphuric acid is not maintained, the soln. first deposits crystals of ferrous sulphate, then copiapite, and later rhomboclase.

Römerite varies in colour from light to dark chestnut-brown, violet-brown, rust-brown, and yellow. It occurs crystalline in coarse granules, and in tabular crystals parallel to (001); the habit may be monoclinic; and the (100)- and (001)-faces may be striated parallel to their edge of intersection, whilst the brachydome faces are vertically striated. The crystals are triclinic; G. Linck gave for the axial ratios  $a : b : c = 0.96840 : 1 : 2.64250$ , and  $\alpha = 116^\circ 3\frac{1}{2}'$ ,  $\beta = 94^\circ 40\frac{1}{2}'$ , and  $\gamma = 80^\circ 7\frac{1}{2}'$ ; J. Blaas, 0.8791 : 1 : 0.8475, and  $\alpha = 89^\circ 44'$ ,  $\beta = 102^\circ 17'$ , and  $\gamma = 85^\circ 18'$ ; and R. Scharizer gave 1.1751 : 1 : 0.8304, and  $\alpha = 94^\circ 44'$ ,  $\beta = 99^\circ 16'$ , and  $\gamma = 87^\circ 22'$ . The (010)-cleavage is perfect; and, according to J. Grailich, the (100)-cleavage is less distinct. J. Grailich said that the pleochroism  $a$  is rose-red or rust-brown,  $b$  is colourless to rose-red, and  $c$  is pale or dark rust-brown. G. Linck gave  $a$  pale

yellowish-white, *b* darker yellowish-white, and *c* reddish-brown. The optical character is negative; the optic axial angle  $2H_a = 57^\circ 45'$  for Na-light; and the double refraction is small. E. S. Larsen found the index of refraction  $\beta = 1.87$ ; and R. E. Landon gave for the indices of refraction  $\alpha = 1.526$ ,  $\beta = 1.571$ , and  $\gamma = 1.582$ . J. Grailich gave 2.174 for the sp. gr., and G. Linck, 2.102; the hardness is 3.0 to 3.5. J. Grailich found that the crystals are diamagnetic. The salt is readily dissolved by water; the aq. soln. is acidic, and deposits basic salts when heated. According to R. Scharizer, when the aq. soln. of r  merite is evaporated to dryness, the soln. decomposes in accord with the equation:  $3\{\text{Fe}'''\text{Fe}_2''(\text{SO}_4)_4\} = 3\text{FeSO}_4 + 3\{\text{Fe}_2'''\text{SO}_4\}_3 = 3\text{FeSO}_4 + \text{Fe}_4'''\text{S}_5\text{O}_{18}(\text{copiapite}) + \text{Fe}_2'''\text{S}_4\text{O}_{15}(\text{rhomboclase})$ . The presence of an excess of rhomboclase in the soln. does not prevent the decomposition of the r  merite. A mixture of sulphuric acid (37.34 parts) and water (100 parts) dissolves 60.99 parts of r  merite. The stability of a soln. of r  merite is raised in the presence of rhomboclase, and it can exist in a soln. of sulphuric acid in the absence of rhomboclase. The solubility of r  merite in a soln. of rhomboclase is very small. When r  merite is exposed to moist air on a funnel, three-fifths of the original ferrous oxide present as ferrous sulphate remains on the funnel. R. Scharizer found a mineral in the Harz in which part of the ferrous iron is replaced by zinc—*vide supra*, zinc r  merite.

C. Lausen found a mineral which he called **louderbackite**—after G. D. Louderback—occurring in pale, chestnut-brown, crystalline crusts in the mine at Jerome, Arizona, where the pyritic ore was smouldering for years; the crystals are biaxial, and have the composition of **ferrous ferric decasulphate**,  $2\text{FeO} \cdot 3(\text{Fe}, \text{Al})_2\text{O}_3 \cdot 10\text{SO}_3 \cdot 35\text{H}_2\text{O}$ . The sp. gr. is 2.185; the hardness is 2.5 to 3.0; the optical character is negative; and the indices of refraction are  $\alpha = 1.544$ ,  $\beta = 1.558$ , and  $\gamma = 1.581$ . C. Lausen also found under similar conditions, in the same locality, a mineral which he called **guildite**—after F. N. Guild. The chestnut-brown, monoclinic crystals had the composition of **copper ferrous ferric heptasulphate**,  $3(\text{Cu}, \text{Fe})\text{O} \cdot 2(\text{Fe}, \text{Al})_2\text{O}_3 \cdot 7\text{SO}_3 \cdot 17\text{H}_2\text{O}$ . The crystals have the axial ratios  $a:b:c = 1.037:1:1.407$ , and  $\alpha = 74^\circ 43'$ . The cleavages parallel to the base (001), and parallel to the front pinacoid (100), are both perfect. The optical character is positive. The sp. gr. is 2.725, and the hardness 2.5. The indices of refraction are  $\alpha = 1.623$ ,  $\beta = 1.630$ , and  $\gamma = 1.684$ . The birefringence is 0.061. The mineral is pleochroic with  $\beta$  and  $\alpha$  pale yellow, and  $\gamma$  greenish-yellow.

J. A. Poumar  de allowed a warm soln. of 2 parts each of hydrated ferrous and ferric sulphates, and 5 to 6 parts of water to crystallize, and obtained long, pale red needles of the **decahydrate**,  $\text{FeSO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 10\text{H}_2\text{O}$ , which are very soluble in water. A.   tard obtained six-sided plates, the colour of peach-bloom, of **ferrous ferric tetrahydrohexasulphate**,  $\text{FeSO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 2\text{H}_2\text{SO}_4$ , by dissolving eq. quantities of ferrous and ferric sulphates in as little water as possible, adding an excess of conc. sulphuric acid, and heating the mixture to about  $200^\circ$ ; and J. Lefort reported the **tridecahydrate**,  $\text{FeSO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 2\text{H}_2\text{SO}_4 \cdot 13\text{H}_2\text{O}$ , to be formed when a cold soln. of hydrated ferrous oxide in conc. sulphuric acid is allowed to stand for some days, and the white salt separated from the mother-liquor on an asbestos-filter. The product is dissolved in the smallest possible quantity of cold water, and allowed to crystallize. The white salt is very deliquescent, but it is stable in dry air. It gives off water at about  $75^\circ$ , and decomposes at a high temp. into a mixture of ferrous and ferric oxides. H. Chandra could not verify this result. M. Lachaud and C. Lep  rier added ferrous sulphate or ferrous ammonium sulphate to fused ammonium sulphate and insufficient sulphuric acid to convert all the ammonia to the hydrosulphate. The excess of ammonium sulphate is removed by treatment with alcohol. There remain colourless, prismatic needles of **ammonium ferrous ferric octosulphate**,  $4(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$ . The sp. gr. of the salt is 2.02 at  $-10^\circ$ . It dissolves slowly in cold water, and is hydrolyzed into a basic sulphate by boiling water.

S. Breislak observed a dark green mineral at the solfatara near Naples, and it

was called **voltaite** by A. Scacchi. The same mineral was observed near Goslar in the Harz; in the cupriferos pyrites of Rio Tinto, Spain; in the pyritiferous trachyte of Madeni Zakh, in Persia; and at Kremnitz, and Schmöllnitz, in Hungary. Descriptions and analyses were reported by G. Tschermak, J. A. Krenner, H. F. Collins, C. A. Anderson, C. Lausen, J. Blaas, P. A. Dufrenoy, H. Abich, and R. Scharizer, and the results are difficult to represent by a single formula. B. Gössner and M. Arm represented it by:  $\text{K}_2\text{H}_{10}(\text{SO}_4)_6 \cdot 3(\text{Fe}, \text{Al})(\text{OH})_3 \cdot 4\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ . R. Scharizer was able to make the formula fit the analysis by assuming that there are two voltaites, one richer in bases than the other, each with 5 mols. of water of crystallization:



R. Scharizer concluded that natural and artificial voltaites are mixtures of a potassium salt of the acid  $\text{H}_2\text{Fe}_2(\text{SO}_4)_4 \cdot 4 \cdot 33\text{Aq.}$ , or  $\text{H}_6\text{Fe}_6(\text{SO}_4)_{12} \cdot 13\text{Aq.}$  and the acid  $\text{H}_{12}\text{Fe}_4(\text{SO}_4)_{12} \cdot 18\text{Aq.}$  B. Gössner and E. Fell gave the general formula:  $\text{Fe}_4''' \text{R}_5'' \text{R}_2' (\text{SO}_4)_{12} \cdot 16$  to  $18\text{H}_2\text{O}$ . The dehydration curve shows that the loss of water commences at  $200^\circ$ ; there is a break at  $200^\circ$  when about 7 mols. of water are lost. The losses with two samples were:

	170°	190°	200°	220°	240°	270°	280°	350°	440°
Loss	0.07	0.31	5.84	6.24	7.50	11.59	12.04	12.80	15.09 per cent.

B. Gössner and M. Arm obtained the following losses (time in hours in brackets):

	100° (20)	150° (30)	200° (40)	225° (50)	300° (60)
Loss	0.70	0.85	1.6	5.3	13.9 per cent.

so that at  $200^\circ$ , the crystals appear turbid; and the water is expelled above this temp. They consider that the water is mainly present as water of crystallization, and represent the formula:  $\text{K}_2\text{H}_4(\text{SO}_4)_3 \cdot 3\text{Fe}(\text{OH})(\text{SO}_4) \cdot 4\text{FeSO}_4 \cdot 10\text{H}_2\text{O}$ . B. Gössner and T. Bäuerlin gave:  $[\text{KH}_5(\text{SO}_4)_3]_2[(\text{Fe}, \text{Al})(\text{OH})_3][\text{FeSO}_4]_4 \cdot 4\text{H}_2\text{O}$ .

H. Abich obtained a salt resembling voltaite,  $3\text{FeSO}_4 \cdot 2\text{Fe}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$ , by boiling a mixture of a not too dilute soln. of 16 parts of ferrous sulphate with 1 part sulphuric acid of sp. gr. 1.4, then adding a hot, conc. soln. of 5 to 6 parts of ferric alum, and evaporating the liquid at  $87^\circ$ . A soln. of the powder in acidulated water was evaporated on a water-bath. L. C. A. Barreswil treated a sat. soln. of ferrous sulphate which was oxidized by adding a mixture of sulphuric and nitric acids, and then treated with conc. sulphuric acid without allowing the temp. to rise. A deep blue precipitate is formed which is decomposed by water. J. Blaas, and R. Scharizer obtained voltaite by crystallization from a soln. of its constituent salts containing an excess of sulphuric acid. B. Gössner and co-workers prepared voltaite by mixing 300 c.c. of water and 45 c.c. of sulphuric acid with 60.4 grms. of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , and 6.7 grms. of potassium sulphate together with varying proportions of 39.1 to 84.5 grms.  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ , and 28.5 to 2.5 grms.  $\text{Fe}_2(\text{SO}_4)_3$ , and keeping the liquid at  $80^\circ$  for some days on a sand-bath. The colour of the soln. is first brown, and when sulphuric acid is added, almost black. As the voltaite separates, the mother-liquor becomes almost colourless. If the soln. is kept at ordinary temp., separations other than voltaite occur; and other products are obtained at higher temp., or with soln. containing more than 30 grms. of ferric sulphate, and less than 30 grms. of aluminium sulphate, or with less than 2.5 grms. of ferric sulphate and over 85 grms. of aluminium sulphate. No voltaite was obtained if either the aluminium or the ferric sulphate be omitted altogether. If chromic sulphate be used in place of ferric sulphate, no **chromic voltaite** was formed; nor was a **nickel voltaite** obtained by using nickelous sulphate in place of ferrous sulphate; but with manganous sulphate in place of ferrous sulphate, orange-yellow cubic crystals of **manganese voltaite**,  $2\text{KHSO}_4 \cdot 4\text{H}_2\text{SO}_4 \cdot 4\text{MnSO}_4 \cdot 3\text{Fe}(\text{OH})_3 \cdot 4\text{H}_2\text{O}$ , of sp. gr. 2.62, were formed; and

with cobaltous sulphate, in place of ferrous sulphate, dark red, cubic crystals of **cobalt voltaite**,  $2\text{KHSO}_4 \cdot 4\text{H}_2\text{SO}_4 \cdot 4\text{CoSO}_4 \cdot 3\text{Fe}(\text{OH})_3 \cdot 4\text{H}_2\text{O}$ , of sp. gr. 2.65, were formed. B. Gössner and co-workers obtained a series of voltaites with the iron partly replaced by alumina and containing as bases **thallium ferrous voltaite**, in octahedral, bluish-green crystals of sp. gr. 3.06 to 3.09; **thallium magnesium voltaite**, in cubic—dodecahedra—green crystals of sp. gr. 2.803; **thallium cadmium voltaite**, in cubic—octahedral and dodecahedral—pale green crystals; **rubidium cadmium voltaite**, in cubic, green crystals of sp. gr. 2.990; and **ammonium magnesium voltaite**, in small, green, cubic crystals of sp. gr. 2.375.

Voltaite occurs in dull green, greenish-black, brown, or black cubic octahedral or dodecahedral crystals, or in combinations of these forms belonging to the cubic system. B. Gössner and M. Arm found that the black, cubic crystals of octahedral habit furnish X-radiograms corresponding with a unit cell having the parameter  $a=27.33 \text{ \AA}$ , and containing 20 mols. The sp. gr. is 2.79; C. A. Anderson gave 2.75; C. Lausen, 2.611; and B. Gössner and M. Arm, 2.648 to 2.654; and the hardness 3 to 4. The double refraction is strong; E. S. Larsen found the index of refraction to be 1.602; C. A. Anderson gave 1.604; and C. Lausen, 1.594. There is no pleochroism. Voltaite is sparingly soluble in water, and the aq. soln. deposits crystals of metavoltine, but in the presence of free sulphuric acid, sphæro-crystals, and composite pseudo-cubic crystals of voltaite are deposited.

A. Paulinyi described a mineral which he called *pettkoite*—after B. von Pettko—and which he obtained from Kremnitz, Hungary, but G. Tschermak showed that it is the same mineral species as voltaite. S. Singer described lemon-yellow, microscopic, monoclinic or triclinic, prismatic crystals of the composition  $(\text{K}, \text{Na})_2\text{O} \cdot 2\text{FeO} \cdot 3(\text{Al}, \text{Fe})_2\text{O}_3 \cdot 6\text{SO}_3 \cdot 27\text{H}_2\text{O}$ , occurring at Bauersberg, near Bischofsheim. He called the mineral *plagiocitrite*. The sp. gr. is 1.881. It decomposes on exposure to air, becoming reddish-yellow; it is soluble in water and the soln. has an acidic reaction and deposits hydrated ferric oxide on boiling. Greenish-black, microscopic, probably monoclinic crystals of the composition  $4(\text{K}, \text{Na})_2\text{O} \cdot \text{FeO} \cdot (\text{Fe}, \text{Al})_2\text{O}_3 \cdot 5\text{SO}_3 \cdot 8\text{H}_2\text{O}$ , were found in the same locality. The mineral was called *clinophæite*. Its sp. gr. is 2.979. It dissolves in water with difficulty, and when the soln. is boiled it deposits hydrated ferric oxide. A deep saffron-yellow mineral occurring in the same locality was called *clinoerocite*. The crystals are probably monoclinic, and a qualitative analysis shows that it belongs to this family of salts. A. Schrauf observed a yellowish-grey, compact or crystalline sulphate related to botryogen in the mercury mines of India, Carniola, and he called it *idrizite*. The analysis corresponds with **magnesium ferrous ferric trisulphate**,  $(\text{Mg}, \text{Fe})\text{O} \cdot (\text{Al}, \text{Fe})_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 16\text{H}_2\text{O}$ . Unlike quetenite, it is insoluble in hot and cold water.

P. C. Ray and P. B. Sarkar prepared the salt **ammonium ferric sulphatofluoberyllate**,  $(\text{NH}_4)_2\text{BeF}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ , isomorphous with the alums. The salt was discussed by W. R. C. Curzel, and H. Seifert. N. Bjerrum and G. H. Hansen prepared from ferric sulphate and the chromic dibromotetraaqua-sulphate, a complex **ferric chromic bromosulphate**,  $[\text{CrBr}_2(\text{H}_2\text{O})_4][\text{Fe}(\text{H}_2\text{O})_6](\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ , but the corresponding chloro-compound could not be prepared.

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## § 48. The Iron Carbonates

The early writers referred to a mineral under various terms; thus, in 1565, C. Gesner<sup>1</sup> called it *stahelreich Eisen*; in 1735, C. Linnæus, *ferrum intractibile albicans spathosum*; in 1747, J. G. Wallerius, *minera ferri alba spathiformis*; A. Cronstedt, *Zarn med Kalkjord förenadt*; T. Bergmann, *ferrum cum magnesio et terra calcarea acido aereo mineralisatum*; J. B. L. Romé de l'Isle, *fer spatique*—hence the term *spathic iron ore*; R. Kirwan, *calcareous or sparry iron ore*; J. F. L. Hausmann, *Eisenspath*, and also *spherosiderite*; F. S. Beudant, *siderose*; P. A. Dufrénoy, and A. Breithaupt, *junckérite*—after M. Junckér; E. F. Glocker, *chalybite*; and W. Haidinger, *siderite* for the mineral, from W. Haidinger's term *spherosiderite*. W. Haidinger reserved the latter name for a concretionary variety. F. Slavik discussed the *spherosiderite* of Kirvinna, Silesia; and C. Y. Hsieh, those of the cretaceous coal of China. Some varieties of *siderite* have received special terms. Thus, A. Breithaupt applied the term *oligonspath*, a manganiferous variety, and J. F. L. Hausmann shortened the word to *oligonite*; A. Mayer called a variety from Bleisbach, Siebengebirge, *thomäite*—after K. Thomä; and a magnesium variety, *sideroplesite*. A variety from New Zealand was called *pelosiderite* by F. Zirkel. Impure siliceous and argillaceous varieties are sometimes called *clay ironstone*, or the *black band ores* of the coal measures. The term *spherosiderite* is applied to a variety which occurs in more or less rounded spherules. J. Young observed a variety from Campsie, Scotland, in which the spherules averaged one-

sixteenth of an inch in diameter, and in section they showed layers of ferrous carbonate round a spherical centre in various shades of brown; they also show a radiating crystalline structure.

In 1774, P. Bayen<sup>2</sup> showed that when the mineral is treated with an acid, it gives off a gas, carbon dioxide, and that lime is present in the acid soln.; he also thought that zinc was present. T. Bergman, and B. G. Sage detected manganese in some samples. In 1804, C. F. Bucholz found 59.5 per cent. of ferrous oxide, and 2.5 per cent. of calcium oxide but not manganese. He noted that a gas is given off when the mineral is heated, and that the residue exhibits polar magnetism. In 1806, H. V. Collet-Descotils reported many analyses, and noted the variations in the composition of the mineral. In 1807, C. F. Bucholz and M. H. Klaproth obtained similar results. Analyses reported by C. F. Rammelsberg,<sup>3</sup> C. R. von Hauer and C. von John, K. R. von Hauer, C. von John, H. von Foullon, F. Sandberger, G. Grattarola, A. Brunlechner, G. H. Williams, F. Beyschlag, A. von Elterlin, G. Bodländer, H. Schwager and C. W. von Gümbel, W. Ortloff, F. Gervais, E. Manasse, F. Gonnard, A. Hutchinson, P. A. Dufrénoy, H. How, E. V. Shannon, C. F. Eichleiter, F. Kretschmer, K. A. Redlich, L. Dürr, A. Carnot, A. Gesell, A. Miko, B. Tacke, A. Pattera, F. Seeland, T. G. Clemson, W. F. Hillebrand, M. Ungemach, L. Girolami, J. von Schröckinger, W. T. Schaller, C. Klein, A. Lasard, A. Frenzel, F. Mons, A. Lévy, L. Colomba, R. P. Greg and W. G. Lettsom, A. Russell, C. Palache, V. R. von Zepharovich, F. W. Clarke, D. Stur, S. Nikitin, W. Michailowsky, C. J. B. Karsten, P. Berthier, J. P. J. Monheim, J. Fritsche, E. Glasson, C. Schnabel, H. Vorl, B. Baumgärtel, G. Bischof, S. P. Popoff, L. Dürr, G. A. Kenngott, A. Pleischl, W. Ortloff, W. Heyer, O. Luedecke, A. Sigmund, G. Magnus, P. Poni, S. G. Rosengarten, D. P. McDonald, M. F. Heddle, A. Lacroix, and F. Tucan. The results in the minerals of a high degree of purity correspond with **ferrous carbonate**,  $\text{FeCO}_3$ . G. Bodländer noted a sample from Neunkirchen, Siegen, with 3.85 per cent. of cobalt; and W. N. Hartley and H. Ramage, samples of Yorkshire clay ironstone with gallium.

Siderite occurs in crystals which are commonly rhombohedral, with the faces more or less curved and built up of smaller crystals. The mineral may also occur in cleavable masses, it may be sub-fibrous or it may occur in silky fibres. It may occur in coarse-grained or fine-grained masses, or in concretionary—botryoidal or globular—forms—e.g., J. F. L. Hausmann's sphaeroiderite—and it may have a scaly or fibrous structure. It may appear oolitic like oolitic limestone; and it may be compact and earthy owing to associated clay or sand as in clay ironstone. The colour is rarely white, and it may appear to be ash-grey, yellowish-grey, greenish-grey, grey, brown, brownish-red, pink, and, in rare cases, green. The colour is produced by impurities. Besides ferrous carbonate of a high degree of purity, one group of siderites may contain several per cent. of manganese carbonate—*manganese siderites*—and the colour has then a yellowish tinge or it may be flesh-red or iron-red; another group may contain several per cent. of magnesium carbonate—*magnesium siderites*—and very little manganese carbonate; another group may contain as much as 20 per cent. of calcium carbonate—*calciferous siderites*; and yet another may contain relatively large proportions of both calcium and magnesium carbonates—*dolomitic siderites*. The iron, calcium, magnesium, and manganese carbonates are isomorphous, and miscible in all proportions, so that the siderites may pass into ferruginous calcespar, ferruginous rhodochrosite, and ferruginous magnesite—e.g., a ferruginous dolomite is called ankerite. *Boxwork siderite*, so named from its structure and appearance, was described by Y. S. Bonillas and co-workers, and by C. Trischka and co-workers.

It was shown in connection with limonite, and bog-iron ores, that waters carrying iron salts in the presence of much carbonic acid, or decaying organic matter, deposit the iron in the form of siderite, and if the conditions are such that air has free access, limonite may be formed. In some cases the deposition is effected by the so-called iron bacteria. If the iron carbonate is deposited from muddy

waters, salt will be associated with the carbonate, and clay ironstone, or black band ores will be formed. This subject has been discussed by F. M. Stappf,<sup>4</sup> E. Kohler, H. Sjögren, K. A. Redlich, J. S. Newberry, A. von Schouppe, J. H. L. Vogt, J. W. Gruner, H. Bücking, W. Reinders, B. Baumgärtel, B. Tacke, A. Gärtner, J. Beyschlag, E. J. Moore, R. Canaval, J. M. van Bemmelen, C. L. Dake, A. Brunlechner, and G. R. van Hise. Siderite may also be formed by an exchange of bases when soln. of iron salts act on limestones, or other carbonate rocks. H. C. Sorby, J. P. Kimball, and L. Dieulafait showed that this may occur by the action of ferrous sulphate soln. on calcium carbonate; while H. C. Sorby, G. Keller, J. N. von Fuchs, J. von Kobell, and H. Demarçay showed that with soln. of ferric sulphate, hydrated ferric oxide is precipitated. J. M. van Bemmelen added that in some cases the deposit which is formed is **colloidal ferrous carbonate**—e.g., the siderite in the peat of the moors in the south-east of Drenthe, Holland. This subject was also discussed by W. Reinders, and A. Gärtner. R. J. Hartman and co-workers obtained periodic precipitations of ferrous carbonate.

In illustration of the formation of siderite in nature, J. R. Blum<sup>5</sup> described pseudomorphs of siderite after galena; H. A. Miers, pseudomorphs after bismuth glance; J. R. Blum, and R. P. Greg and W. G. Lettsom, after fluorite; J. R. Blum, A. Frenzel, G. Greim, F. Gonnard, after calcite; J. R. Blum, after dolomite; J. R. Blum, G. Greim, and A. Frenzel, after aragonite; J. R. Blum, and R. P. Greg and W. G. Lettsom, after barytes; and J. H. Collins, after gypsum.

**The formation and preparation of ferrous carbonate.**—When a soln. of a ferrous salt is treated with an alkali carbonate, a white hydrated ferrous carbonate is precipitated. On exposure to air, the precipitate soon acquires a green colour, and it afterwards becomes brown, owing to oxidation. Alkali hydrocarbonates furnish a similar precipitate with soln. of ferrous sulphate provided that the soln. are not too dilute. If they are dilute, some ferrous salt is retained in solution, but is deposited when the soln. are boiled. It is difficult to wash and dry the precipitate without oxidation. The preparation of the carbonate by these methods has been discussed by F. Arcularius,<sup>6</sup> C. Birkholz, W. Petrascheck, L. Bley, C. H. Bolle, R. Brandes, E. Braun, A. Buchner, C. F. Bucholz and J. W. Döbereiner, M. Daum, F. Fölix, P. Groth, H. Hager, G. A. Kennigott, C. Klauer, A. Lacroix, A. Meillet, C. F. Mohr, H. Reinsch, W. T. Schaller, F. W. Schmidt, G. Schmidt, A. G. Vallet, H. Wilkens, and G. C. Wittstein. R. E. Brewer and G. H. Montillon precipitated ferrous carbonate by adding sodium carbonate to a soln. of ammonium ferrous sulphate in an atm. of hydrogen; washed the white or greenish-white precipitate with water saturated with hydrogen; and preserved the product under water similarly treated. The yield was smaller when sodium hydrocarbonate was the precipitating agent. H. J. Smith obtained a white carbonate by placing equimolar proportions of solid ferrous sulphate and sodium hydrocarbonate in a steel bottle, and displacing the air by carbon dioxide. Water saturated with carbon dioxide was added, and the bottle closed by a plug attached by a suitable valve to a cylinder of compressed carbon dioxide. The valve was closed when the press. in the bottle had attained 400 lbs. and the bottle was kept at 100° for several days. The precipitate was filtered in an atm. of carbon dioxide, and washed with water sat. with carbon dioxide. A similar process was employed by A. Meillet. The analyses of J. B. Berthemot, H. Diesel, F. J. Malaguti, G. Schmidt, H. Schütte, B. Tacke, G. C. Wittstein, and F. Massieu show that water is only mechanically associated with precipitated ferrous carbonate; no definite hydrate has been prepared. R. C. Wells discussed the fractional precipitation of ferrous carbonate from soln. of ferrous salts mixed with salts of copper, calcium, zinc, cadmium, lead, and nickel. H. de Sénarmont heated a soln. of ferrous sulphate with sodium carbonate in a sealed tube 150° or over, or else a mixture of ferrous chloride and calcium carbonate at 135° to 180°, for 12 to 18 hrs., and obtained a greyish-white, arenaceous material which consisted of crystals of siderite. A. Buchner previously prepared ferrous carbonate by the action of powdered calcite on a soln. of ferrous chloride in a sealed



tube; and F. Hoppe-Seyler heated to  $200^{\circ}$  a soln. of ferrous sulphate with an excess of calcium carbonate in a tube from which oxygen had been displaced, and obtained microscopic crystals of siderite. A. Bruzs found that the ferrous carbonate prepared by H. de Sénarmont's process loses 20 per cent. of its carbon dioxide when it is dried. As indicated above, H. C. Sorby, and others have observed that when calcite, aragonite, or witherite is immersed in a sealed tube at  $100^{\circ}$  to  $150^{\circ}$ , there is a slow exchange of bases, so that in about a month, crystals of siderite are formed. The formation of ferrous carbonate by rusting iron was discussed by F. C. Calvert, and G. T. Moody—*vide supra*.

A. Meillet obtained white, compact ferrous carbonate by the action under press. of carbon dioxide on precipitated ferrous carbonate containing more or less ferrous hydroxide. F. K. Cameron and W. O. Robinson observed that at  $0^{\circ}$ , and under a press. of 76 to 274 cm., carbon dioxide converts moist ferrous hydroxide into carbonate, but not into hydrocarbonate—*vide infra*. P. N. Raikow passed carbon dioxide into water with freshly-precipitated ferrous hydroxide in suspension, and found that 13 to 22 per cent. more carbon dioxide was absorbed than is necessary for the formation of ferrous carbonate. A. Smits, and W. P. Jorissen and J. Rutten observed that ferrous sulphide is slowly transformed by carbon dioxide into ferrous carbonate. J. Durochet, and R. Brauns described the formation of crystals of siderite by the action of the vapour of ferrous chloride on ammonium carbonate in an iron tube at a red-heat.

L. Bourgeois failed to obtain ferrous carbonate by heating a ferrous salt soln. with urea at about  $140^{\circ}$ . A. Michaelis obtained ferrous carbonate by boiling ferrous oxalate with a soln. of potassium hydrocarbonate; and V. Volmar, by the action of ultra-violet light on a 1 per cent. soln. of ferric tartrate—the ferrous carbonate was mixed with ferrous hydroxide. F. Haber and F. Goldschmidt electrolyzed soln. of potassium, sodium, and calcium hydrocarbonates between iron electrodes with a diaphragm-cell, at  $20^{\circ}$ , and obtained in the anode compartment greyish-white ferrous carbonate.

A. Flüge obtained ferrous carbonate for medicinal purposes by triturating a cold mixture of alkali hydrocarbonate and ferrous sulphate with glycerol or a sugar soln.:  $\text{FeSO}_4 + 2\text{KHCO}_3 = \text{FeCO}_3 + \text{K}_2\text{SO}_4 + \text{H}_2\text{O} + \text{CO}_2$ . Other processes for obtaining an analogous product were described by O. Anselmino and E. Gilg, M. Tennenbaum and C. von Eweye, and J. C. Krantz. The object is to retard the oxidation of the ferrous carbonate in air—*vide infra*.

**The physical properties of ferrous carbonate.**—The colour of ferrous carbonate is white, but by oxidation it acquires a green tinge and later becomes brown. Siderite may occur in nature, white, ash-grey, green, greenish-grey, yellowish-grey, brown, and brownish-red. The powder is white. Siderite occurs crystalline; in cleavable, fine or coarse granular masses; in botryoidal and globular forms with a sub-fibrous or silky fibrous structure; and in compact or earthy masses. The crystals are commonly rhombohedral, and their faces are often curved and built up of sub-individuals. W. H. Wollaston gave for the axial ratio of siderite  $a : c = 1 : 0.81841$ ; A. Breithaupt gave  $1 : 0.8191$  and  $\alpha = 103^{\circ} 41'$ ; and E. Mitscherlich gave  $a : c = 1 : 0.81840$  at ordinary temp., and  $1 : 0.81912$  at  $100^{\circ}$ . F. Rinne found that the angle  $\alpha$  changes  $3.1'$  per  $100^{\circ}$  rise of temp. so that for the normal angle, at :

	$-165^{\circ}$	$60^{\circ}$	$22^{\circ}$	$104^{\circ}$	$200^{\circ}$	$302^{\circ}$	$385^{\circ}$
$\alpha$	$72^{\circ} 59' 51''$	$73^{\circ} 3' 7''$	$73^{\circ} 3' 50''$	$73^{\circ} 6' 42''$	$73^{\circ} 10' 1''$	$72^{\circ} 13' 41''$	$72^{\circ} 16' 46''$

The value of  $a : c$  at  $-165^{\circ}$  is  $1 : 0.8184$ ; at  $22^{\circ}$ ,  $1 : 0.8194$ ; and at  $385^{\circ}$ ,  $1 : 0.8235$ . Observations on the crystals were made by A. Breithaupt, G. Cesaro, A. des Cloizeaux, L. Colomba, V. Goldschmidt, M. Henglein, G. A. Kennigott, C. Klein, A. de Klerk and V. Goldschmidt, W. Jansen, A. Lacroix, A. Lévy, E. Manasse, W. H. Miller, C. Palache, A. Russell, W. T. Schaller, and L. J. Spencer. Siderite is uniaxial, but A. Madelung observed a sample from Neudorf, Harz, which was feebly

biaxial. Siderite belongs to an **isomorphous family**,  $R''CO_3$ , where R may denote Ca, Sr, Ba, Mg, Zn, Pb, Mn, Fe, and Co. The isomorphism was discussed by G. Bilibin, P. Gaubert, W. Diesel, K. Grünberg, and H. de Sénarmont. This is exemplified by the minerals *bräunerite*, *roeperite*, *masitite*, and *sideroplesite*,  $(Mg,Fe)CO_3$ ; *manganocalcite*, and *spartoite*,  $(Ca,Mn,Fe,Mg)CO_3$ ; *rhodochrosite*, *manganese spar*, and *dialogite*,  $(MnFe)CO_3$ ; *iron zinc spar*,  $(Zn,Fe)CO_3$ ; *monheimite*,  $(Zn,Mn,Fe)CO_3$ ; and *ankerite*,  $(Ca,Mg,Fe)CO_3$ . W. Diesel observed solid soln. of ferrous and calcium carbonates of the vaterite type, and hence H. E. Boeke inferred that there is an unstable modification of ferrous carbonate which has not yet been isolated, and whose sp. gr., by extrapolation, is near 3.4. The colloidal form has been indicated above. The **twinning** of the rhombohedral crystals occurs about the (01 $\bar{1}$ 2)-plane, often with enclosed twinning lamellæ; the subject was discussed by E. Ammermann, G. A. Kenngott, and L. J. Spencer. The (0001) **cleavage** is perfect. A. Johnsen found that, as with calcite, the (10 $\bar{1}$ 1)-plane is a **gliding plane**. The **corrosion figures** are in part symmetric and in part asymmetric, and they were examined by H. Baumhauer, A. P. Honess, W. T. Schaller, and G. Tschermak. I. N. Stransky and K. Kubelief studied the **growth of the crystals**; P. Groth, parallel **over-growths** with calcite, and S. Kreutz, over-growths with lithium nitrate. The **X-radiograms** of siderite were investigated by W. Jansen, W. L. Bragg and co-workers, P. P. Ewald, and P. Niggli. According to R. W. G. Wyckoff, the elementary rhombohedral cell has the parameter  $a=6.04$  Å,  $\alpha=47^\circ 46'$ ; G. Natta:  $a=5.82$ , and  $\alpha=47^\circ 45'$ ; and P. Niggli calculated that there are 4 mols. per cell. the edge of the cell is  $5.94 \times 10^{-8}$  to  $5.99 \times 10^{-8}$  cm., the vol. of the cell is  $194.9 \times 10^{-24}$  c.c., and the vol. of the mol.  $FeCO_3$  is  $48.75 \times 10^{-24}$  c.c. The structure of the  $CO_3$ -group was discussed by C. Schaefer and co-workers, and J. E. Lennard-Jones and B. M. Dent; the arrangement of the electrons, by M. L. Huggins; the structure of the lattice by W. L. Bragg and S. Chapman, and S. Chapman and co-workers; the free energy of formation of the crystals from the elements, by J. L. Buchan; and the work of separating  $Fe^{++}$  from  $CO_3^{--}$ -ions, by J. E. Lennard-Jones and B. M. Dent. P. Niggli studied the **electronic structure**.

The **specific gravity** of pure siderite, extrapolated by E. T. Wherry and E. S. Larson, is 3.96; W. E. Ford gave 3.633 to 3.951 for samples of siderite with 78.2 to 95.9 per cent.  $FeCO_3$ ; H. Kopp gave 3.796 at  $0^\circ$ ; P. A. Dufrenoy, 3.815; N. Sundius, 3.927; A. Breithaupt, 3.698; F. E. Neumann, 3.872; A. Hutchinson, 3.936 to 3.938; A. Lemke and W. Biltz, 3.832 to 3.856; and E. Madelung and R. Fuchs, 3.7718. The effect of impurities is shown in Table XCV by P. Niggli; K. Grünberg's curve for the sp. gr. of mixtures of ferrous and calcium carbonates is shown in Fig. 679. I. I. Saslawsky calculated a value for the contraction which occurs when ferrous carbonate is formed from its elements. A. Lemke and W. Biltz studied this subject. The **hardness** of siderite on Mohs' scale is 3.5 to 4. F. Pfaff found that if the hardness of talc be unity, that of siderite on the (0001)-face is 32, and on the (10 $\bar{1}$ 1)-face, 53. E. Madelung and R. Fuchs gave  $0.0_999$  for the coeff. of **compressibility** in megabars per sq. cm. L. H. Adams and E. D. Williamson gave  $\beta=0.0_660$ ; and for the **bulk modulus**,  $K \times 10^{-6}=1.67$ ; and the **rigidity**,  $R \times 10^{-6}=0.91$ .

H. Fizeau found the coeff. of **thermal expansion** in the direction of the  $a$ -axis to be 0.00001918, and perpendicular to that axis, viz. the  $c$ -axis, 0.00000605, at  $40^\circ$ . F. Pfaff gave 0.000005388 for the  $c$ -axis, and 0.000016133 for the  $a$ -axis from  $0^\circ$  to  $100^\circ$ . For the coeff. of cubical expansion, H. Kopp gave 0.000035 between  $14^\circ$  and  $45^\circ$ ; and F. Pfaff, 0.00002688 between  $0^\circ$  and  $100^\circ$ . Observations were made by O. Hülsmann and W. Biltz. E. Jannettaz gave 1.06 for the sq. root of the ratio of the **thermal conductivity** parallel and vertical to the chief axes. F. E. Neumann

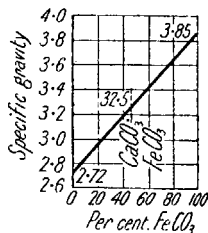


FIG. 679.—The Specific Gravities of Solid Soln. of Calcium and Ferrous Carbonates.

found the **specific heat** of siderite to be 0.182 to 0.183; H. Kopp gave 0.166 between 17° and 46°; H. V. Regnault, 0.1934 between 9° and 98°; and F. Ulrich and E. Wollny, 0.1793. C. Pape made some observations on H. V. Regnault's results. W. A. Roth and W. Bertram found the mean sp. ht. between 20.5° and 95° to be 0.196; and the mean molecular heat, 22.72 at 100°. C. T. Anderson gave for  $C_p$  at

	-218.9°	-205.6°	-182.2°	-141.2°	-89.0°	-32.6°	13.0°	23.3°
$C_p$	4.117	5.714	8.489	12.14	15.15	17.83	19.34	19.57

At the beginning of the nineteenth century, C. F. Bucholz, and M. H. Klaproth noted that the **thermal decomposition** of siderite at a red-heat, and out of contact with air, results in the evolution of a combustible gas, presumably carbon monoxide, and the residual oxide is magnetic, presumably  $\text{Fe}_3\text{O}_4$ . The carbon monoxide is formed by the reduction of carbon dioxide by ferrous oxide at a red-heat. This was confirmed by the work of J. W. Döbereiner, J. N. von Fuchs, F. J. Malaguti, A. Krämer, E. Glasson, S. de Luca, and I. L. Bell. J. W. Döbereiner gave  $5\text{FeCO}_3 = 3\text{FeO} + \text{Fe}_2\text{O}_3 + 4\text{CO}_2 + \text{CO}$ . J. A. Hedvall observed that with 4 hrs. heating at 700°, a basic ferrous carbonate gave ferric oxide. K. Busz, W. Jung, J. J. Nöggerath, and H. Pohligh also observed that siderite appears to have been converted into magnetite when it has been in contact with basalt intrusions. G. C. Wittstein observed that when hydrated ferrous carbonate is heated out of contact with air, the ferrosic oxide which is formed may be pyrophoric. H. Moissan observed that ferrosic oxide is formed when ferrous carbonate is heated out of contact with air, and when carbon dioxide is passed over ferrous oxide, carbon monoxide and ferrosic oxide are formed. Hence it is probable that the ferrous carbonate first splits into ferrous oxide and carbon dioxide, and that these react on one another in accord with:  $2\text{FeO} + \text{CO}_2 = \text{CO} + \text{Fe}_2\text{O}_3$ . If ferrous carbonate be slowly heated in a current of nitrogen, ferrosic oxide is produced, and if rapidly heated, pyrophoric ferrous oxide is formed.

A. Knop observed that the thermal decomposition of ferrous carbonate begins at about 350°. K. Friedrich and L. G. Smith found that the decomposition of siderite begins at about 400°, and proceeds rapidly at 460° to 500°. H. Wölbling said that the decomposition begins at about 220°, but only becomes appreciable at about 300°; the reaction is favourably influenced by water vapour; W. Hempel and C. Schubert, that the reaction begins at 470°, and is completed at 880°; J. A. Hedvall, that in nitrogen, siderite begins to decompose at 195°; H. Schneiderhöhn, that the decomposition is perceptible between 300° and 400°; and A. Gautier and P. Clausmann that siderite slowly decomposes at 300°, and rapidly at 400° in accord with:  $3\text{FeCO}_3 = \text{Fe}_3\text{O}_4 + 2\text{CO}_2 + \text{CO}$ . E. A. Wülfing observed that siderite of a high degree of purity lost 31.71 per cent. in weight on heating it 2 hrs. at 500°, and 32.61 per cent. when heated for 10 mins. over a blast-flame. F. Duftschmidt observed that the reactions which occur in an inert gas can be symbolized:  $\text{FeCO}_3 = \text{FeO} + \text{CO}_2$  and  $3\text{FeO} + \text{CO}_2 = \text{Fe}_3\text{O}_4 + \text{CO}$ . In a current of carbon dioxide mixed with nitrogen, when the partial press. of the carbon dioxide is 710 mm., siderite begins to decompose at about 450°; the speed of the reaction rapidly rises with the temp.; in nitrogen alone, the mineral darkens at 300°, and at 350° the evolution of carbon dioxide is perceptible. Air accelerates the decomposition more than does nitrogen. In a current of carbon dioxide, ferrosic oxide is produced at 550°, and at higher temp. ferric oxide is formed. In a current of air ferric oxide is produced. H. Fleissner added that in steam, the ferrous carbonate decomposes at 250°, in air at 420°, in nitrogen at 440°, and in carbon dioxide at 500°. L. Gruner studied the decomposition of the carbonate in carbon dioxide; and H. Fleissner and F. Duftschmidt, in carbon monoxide, producer gas, and hydrogen. According to B. Bruzs, the thermal decomposition of siderite in the interval 491° to 581° is unimolecular,  $dx/dt = ae^{-kt}$ , where  $a$  is the initial velocity when  $t=0$ ; and  $k$  is the velocity constant:

	491°	511°	521°	531°	541°	550°	561°	573°	581°
$k$	0.00805	0.0221	0.0442	0.0851	0.191	0.352	0.607	0.989	1.472

The velocity constant is abnormal at 491°, and between 445° and 495°, the velocities are low. It is inferred that within this range, the velocity constant remains unchanged, whilst the active mass increases with temp. Whilst the mineral form can be completely decomposed at 495°, the synthetic form can be decomposed at 340°—when the press. of carbon dioxide is 760 mm. The values of  $k$  are 0.0110 at 340°, 0.0152 at 350°, and 0.0239 at 360°. The critical increment,  $E$ , calculated from  $\log(k_1/k_2) = (E/R)(T_2^{-1} - T_1^{-1})$ , is 85,500 cal. for siderite between 501° and 561°, and 30,700 cal. for the synthetic carbonate between 340° and 360°. The influence of the grain-size of the carbonate on the speed of decomposition was examined by H. Fleissner, and B. Bruzs; and W. A. Noyes and W. E. Vaughan, and K. Fischbeck and K. Schnaidt discussed the reaction.

M. Berthelot calculated for the **heat of formation** of precipitated ferrous carbonate,  $(\text{Fe}, \text{C}, 1\frac{1}{2}\text{O}_2) = 178.8$  Cals.; H. le Chatelier gave for the crystallized carbonate, 184.5 Cals.; and with carbon as graphite, W. A. Roth and co-workers gave 171.7 Cals. H. le Chatelier also gave for the crystalline carbonate and gaseous carbon dioxide,  $(\text{FeO}, \text{CO}_2) = 25.2$  Cals., and W. A. Roth, and D. Müller 13.4 Cals. Values were also calculated for the thermal decomposition by B. Bruzs—*vide supra*. M. Berthelot gave for the **heat of neutralization** with dissolved carbon dioxide,  $\{\text{Fe}(\text{OH})_2, \text{CO}_2\} = 10.0$  Cals., and with gaseous carbon dioxide, 15.6 Cals. W. A. Roth found that the **heat of oxidation**:  $3\text{FeCO}_3 + \frac{1}{2}\text{O}_2 = \text{Fe}_3\text{O}_4 + 3\text{CO}_2 + 33.4$  Cals. J. L. Buchan gave -175,000 cal. per mol for the **free energy** calculated from the heat of formation of the crystalline carbonate from its elements; and -151.520 cal. per mol when calculated from the lattice constants. C. T. Anderson gave 22.2 for the **entropy**. J. E. Lennard-Jones and B. M. Dent calculated the work of separating  $\text{Fe}^{++}$ -ions from  $\text{CO}_3^{--}$ -ions in the crystal lattice to be 759 to 765 cal. per mol.

A. Hutchinson found that the **indices of refraction** of siderite from Camborne, Cornwall, with respectively 98.43, 1.82, 0.18, and 0.26 per cent. of ferrous, manganese, calcium, and magnesium carbonates, to be:

	Li-	Na-	Tl-light
$\omega$ . . . .	1.8642 to 1.8655	1.8722 to 1.8734	1.8798 to 1.8812
$\epsilon$ . . . .	1.6278 to 1.6306	1.6310 to 1.6342	1.6344 to 1.6373

W. Orloff observed a pale yellow siderite from Wolfsberg, Harz, to have  $\omega = 1.93409$ , and  $\epsilon = 1.62185$ . The results of W. E. Ford, H. von Philipsborn, P. Gaubert, and E. T. Wherry and E. S. Larsen were collected by P. Niggli in Table XCV.

TABLE XCV.—INDICES OF REFRACTION AND SPECIFIC GRAVITIES OF SIDERITES.

Locality	Composition				Sp. gr.	Indices of refraction	
	$\text{FeCO}_3$	$\text{MnCO}_3$	$\text{MgCO}_3$	$\text{CaCO}_3$		$\omega$	$\epsilon$
Ivigtut *	95.9	4.1	—	—	3.951	1.872	1.634
Ivigtut . . . .	93.49	5.16	0.62	0.37	3.940	1.871	1.631
Spokane . . . .	93.16	trace	1.83	5.13	3.840	1.858	1.622
Mine de Baigorri **	89.08	1.9	7.56	—	—	1.8416	1.620
Roxbury, Conn.*	83.6	5.7	9.1	1.6	3.793	1.847	1.613
Neudorf *	77.2	15.8	6.6	0.4	3.813	1.849	1.615
Bindt *	76.8	4.7	17.9	0.6	3.707	1.838	1.603
Bindt *	73.2	2.2	73.3	1.3	3.633	1.830	1.596
St. Pierre **	c. 73	—	—	—	—	1.820	1.609
D'Allevard **	c. 73	—	—	—	—	1.8056	1.6012
D'Allevard **	—	—	—	—	—	1.7959	1.5982
Vizille **	70.24	1.62	26.28	—	—	1.814	1.586

W. E. Ford's results are marked \*, and those of P. Gaubert \*\*. Observations were also made by N. Sundius, and W. A. Wooster. By extrapolation, E. T. Wherry

and E. S. Larsen found that for ferrous carbonate,  $\omega=1.875$ , and  $\epsilon=1.635$ ; and W. E. Ford,  $\omega=1.875$  and  $\epsilon=1.633$ . W. L. Bragg calculated for the molecular refraction, 13.48 from  $\omega$  and 10.57 from  $\epsilon$ . S. Procopiu found that powdered siderite suspended in organic liquids, exhibits **double refraction** in magnetic and electric fields. The double refraction of abnormal crystals, observed by A. Madelung has been previously mentioned. J. Chaudier also found that suspensions of powdered siderite in carbon disulphide exhibit an optical and an electrical birefringence.

L. B. Morse measured the **reflecting power** of the crystals for ultra-red light between  $5\mu$  and  $16\mu$ , and maxima were found for  $6.60\mu$ ,  $11.47\mu$ , and  $13.9\mu$ ; whilst C. Schaefer and M. Schubert observed maxima at  $6.77\mu$ ,  $11.53\mu$ , and  $13.54\mu$  with ordinary light, and maxima with  $\omega$ -light were observed at  $6.77\mu$  and  $13.54\mu$ , and with  $\epsilon$ -light, a maximum at  $11.53\mu$ . Observations were also made by C. Schaefer and co-workers, W. W. Coblenz, W. Schmidt, and T. Liebisch and H. Rubens. The **absorption spectrum** of ultra-red light was measured by W. W. Coblenz between  $1.5\mu$  and  $6\mu$ ; and C. Schaefer and co-workers observed the results summarized in Fig. 680, for a plate cut perpendicular to the  $c$ -axis. The absorption with wavelength below  $9\mu$  is ascribed to the presence of the  $\text{CO}_3$ -radicle being characteristic of the carbonates of calcium, barium, magnesium, and lead. Observations were made by E. K. Plyler.



FIG. 680.—The Transmission of the Ultra-red Rays of Siderite.

E. Engelhardt observed that in ultra-violet light, some samples of siderite show a feeble, white **luminescence**, but not **phosphorescence**. C. Doelter observed that **radium radiations** deepen the colour of yellow siderite to brownish-yellow, and a similar change of colour occurs on exposing the crystals to air, and it is due to oxidation, so that radium rays accelerate the speed of aerial oxidation. E. Baur found that the **photochemical transformation** of ferrous carbonate to oxalate:  $2\text{FeCO}_3 = (\text{FeO})_2\text{C}_2\text{O}_4$ , proceeds neither with nor without sensitizers.

G. Meslin found that a suspension of siderite in carbon disulphide exhibits **magnetic dichroism**—*vide supra*, ferric oxide. L. Graetz found that the **electrical dispersion** of siderite is positive. H. Knoblauch observed the **dielectric polarization** of crystals of siderite. T. Liebisch and H. Rubens found that the **dielectric constant** of siderite is 7.8 for the ordinary ray, and 6.0 for the extraordinary ray; whilst W. Schmidt found for the extraordinary ray 6.85 parallel to the  $c$ -axis, and 7.85 normal to the  $c$ -axis. W. A. D. Rudge observed the positive **electrification** of siderite when the dust is blown through a wire gauze. A. Abt gave 7154 ohms for the **electrical resistance** of a cm. cube of siderite. J. Königsberger discussed the **electrical conductivity** of ferrous carbonate. T. Liebisch calculated from J. Tyn-dall's observations that the ratio of the attractive force of two spheres of siderite between the poles of an electromagnet in directions parallel and vertical to the isotropic axes is as 100 : 71. T. W. Case observed no change in the resistance on exposure to light.

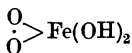
M. Faraday showed that siderite is paramagnetic, and he examined the effect with heated crystals. G. Foëx found the sp. **magnetic susceptibility** of siderite parallel and vertical to the chief optical axis to be :

	$-186^\circ$	$-73^\circ$	$19.5^\circ$	$42.8^\circ$	$62.1^\circ$	$77.7^\circ$	$102.5^\circ$	$128.5^\circ$
$\chi$ { Parallel.	581.16	231.3	142.6	129.8	120.9	111.9	105.3	97.0
Vertical.	180.3	111.4	84.2	79.4	76.0	72.4	69.4	66.0

Above  $-73^\circ$ , the sp. susceptibility is a linear function of the temp., and the lines for  $\chi$  taken parallel and perpendicular to the chief axis are parallel. F. Stutzer and co-workers gave  $332 \times 10^{-6}$  for the coeff. of magnetization; and W. R. Crane,

$1.86 \times 10^{-6}$  for the magnetic susceptibility. The subject was studied by G. Dupouy, L. Pauling and M. L. Huggins, and K. S. Krishnan and co-workers; and the paramagnetic rotation by J. Becquerel and co-workers. H. A. J. Wilkens and H. B. C. Nitze placed siderite amongst the minerals susceptible to attraction in magnetic separations, as in the separation of siderite from zinc blende discussed by E. Clark, G. Prus, M. Bellom, and G. Gromier.

**The chemical properties of ferrous carbonate.**—Y. A. Ravich-Shcherbo, and H. Schneiderhöhn studied the weathering of siderite under the influence of microorganisms. When siderite is heated to redness in **hydrogen**, H. Fleissner and F. Duftschmidt found that carbon dioxide and monoxide and water are evolved, and the residue contains some metallic iron. A current of hydrogen accelerates the thermal decomposition of siderite by carrying the carbon dioxide away from the seat of the reaction. Siderite becomes brownish-red or brownish-black on exposure to **air**, owing to the oxidation of the iron as it passes to limonite; and by a subsequent loss of water it may pass to hæmatite or magnetite. The deoxidation in the latter case may be assisted by the presence of organic matter. In illustration of some of the changes which siderite may undergo in nature, J. R. Blum, M. von Sillem, A. Breithaupt, and R. Nositz mentioned that pseudomorphs of hæmatite after siderite may occur; A. Breithaupt, J. R. Blum, and C. O. Trechmann, of goethite; M. von Sillem, J. R. Blum, E. Weinschenk, G. Grattarola, H. Höfer, J. Samoiloff, A. Schmidt, and E. F. Glocker, of limonite; J. R. Blum, of magnetite; and J. R. Blum, and A. Breithaupt, of chlorite. H. de Sénarmont observed that dry, white ferrous carbonate does not change in dry air, but it slowly coloured in moist air; and S. de Luca found that white and dry ferrous carbonate can be preserved indefinitely in sealed tubes, but with the entry of air and moisture, it is slowly converted into hydrated ferric oxide. A. Krause also noted that precipitated ferrous carbonate, neutral to litmus, is slowly oxidized in air to hydrated ferric oxide almost free from carbon dioxide. G. T. Moody made an analogous observation. The subject was studied by J. Klärning, and F. Duftschmidt. For the decomposition of ferrous carbonate when heated in air, *vide supra*. According to C. Klauer, the moist carbonate becomes dry after exposure to the air for a few days, and is converted into ferric oxide; the oxidation of the partially-dried powder in air may proceed so quickly that the powder becomes hot, and gives off steam. If the moist powder be mixed with sugar, it acquires a coating of syrup which renders it more permanent. R. Phillips also noted how the presence of sugar retards the oxidation of the carbonate, even when it is held in soln. by water impregnated with carbon dioxide. A. Bickel and C. van Eweyk studied the subject. According to G. Just, in the oxidation of ferrous carbonate in soln. in carbonated water:  $4\text{Fe}(\text{HCO}_3)_2 + 2\text{H}_2\text{O} + \text{O}_2 = 4\text{Fe}(\text{OH})_3 + 8\text{CO}_2$ , the reaction is bimolecular, but the oxygen in the first stage of the process acts molecularly:  $\text{Fe}(\text{HCO}_3)_2 = \text{Fe}(\text{OH})_2 + 2\text{CO}_2$ , and there may be produced an intermediate "moloxide":



Freshly-precipitated ferrous carbonate takes up oxygen from the air, which thereby becomes activated so that, as shown by O. Baudisch and his fellow-workers, many organic substances—*e.g.*, lactic acid, sugar, and pyrimidine—are simultaneously oxidized. If the ferrous carbonate be not freshly precipitated, it will be oxidized by air, but the oxygen is not activated, and pyrimidine, for instance, is not oxidized. The facility of activating the oxygen may last for a few seconds or minutes.

According to A. Knop, powdered siderite is decomposed by **water** vapour at about  $100^\circ$  forming carbon dioxide, and with coarse-grained siderite, a little carbon monoxide is formed as well; at a red-heat, carbon dioxide and hydrogen are formed with little or no carbon dioxide. A. Gautier observed that when steam acts on siderite at a red-heat, ferric and ferrous oxides, hydrogen and carbon dioxide are produced. W. Traube and co-workers showed that freshly-precipitated

ferrous carbonate is oxidized by boiling water in the presence of palladium chloride forming hydrogen and carbon dioxide. C. von Hauer said that if carbon dioxide at ordinary press. be passed through water in which iron is suspended, a soln. containing 9.1 parts of  $\text{FeCO}_3$  to 10,000 parts of water is obtained; R. Wagner, that 100 parts of water sat. with carbon dioxide can dissolve 0.72 part of  $\text{FeCO}_3$ , that one part of  $\text{FeCO}_3$  dissolves in 1381 parts of water sat. with carbon dioxide under a press. of 4 to 6 atm.; H. Ehlert and W. Hempel, that a litre of water sat. with carbon dioxide dissolves 6.1907 grms. of freshly-precipitated carbonate under a press. of 2 atm. at  $14^\circ$ ; O. Haehnel, that 100 grms. of a sat. soln. of ferrous carbonate in water at  $18^\circ$ , and in contact with carbon dioxide at a press. of 1 atm., contain 0.072 gm  $\text{FeCO}_3$ , and if the press. be 5 atm., 0.077 gm.  $\text{FeCO}_3$  dissolves; J. Günzburg, that a litre of water, through which a current of carbon dioxide is continually passed, dissolves 0.504 gm. of precipitated ferrous carbonate at room temp.; A. Cossa, that 10,000 parts of water charged with carbon dioxide at atm. press., dissolve 7.2 parts of siderite at  $18^\circ$ ; J. Ville, that a litre of water charged with carbon dioxide at atm. press., dissolves:

$\text{FeCO}_3$	$15^\circ$	$19^\circ$	$20^\circ$	$24^\circ$
	1.390	1.185	1.142	1.098 grms.

and L. F. Caro, that 10,000 parts of water sat. with carbon dioxide at a press.  $p$  atm., dissolve:

$p$	1	2	3	4	5	6	7	8 atm.
$\text{FeCO}_3$ { at $5^\circ$	3.45	4.21	4.56	5.36	5.74	6.51	6.51	5.51
{ at $20^\circ$	3.25	3.73	4.12	4.59	5.07	5.36	5.84	6.12

J. R. Baylis found that the solubility of precipitated ferrous carbonate,  $S$  parts Fe per million, in water containing  $\text{CO}_2$  parts per million, with the  $\text{H}^+$ -ion conc.  $p_{\text{H}}$  is:

$\text{CO}_2$	8.8	5.0	0	0	0	0
$p_{\text{H}}$	7.2	7.3	8.4	8.6	9.1	9.6
$S$	4.0	1.0	0.10	trace	0.10	trace

The subject has been discussed in connection with the corrosion of iron (*q.v.*) by H. Henecka, M. Rohland, J. Günzburg, etc. J. Tillmans and B. Klarmann, for instance, say that water with over 100 mgrms. per litre of combined carbonic acid will dissolve iron pipes, whilst water with a  $\text{H}^+$ -ion conc. of  $0.3 \times 10^{-7}$  to  $4.0 \times 10^{-7}$  may be considered safe. J. W. Gruner observed that the solubility of siderite in peat-water can be detected after 77 days' exposure, and after 182 days' exposure, the water contains 48 parts of iron per million parts of water. According to J. R. Baylis, the solubility of ferrous carbonate,  $S$  parts Fe per million, in water containing  $\text{CO}_2$  parts per million, in the  $\text{H}^+$ -ion conc.  $p_{\text{H}}$  is:

$\text{CO}_2$	0	0	2.0	13.2	24.0	33.4
$p_{\text{H}}$	9.6	8.0	7.3	7.0	6.7	6.8—
$S$	trace	trace	0.8	6.5	12.0	14.0

It is assumed that normal ferrous carbonate is insoluble in water, but it dissolves if carbonic acid be present. It is assumed that in the presence of carbonic acid, the carbonate is in soln. as ferrous hydrocarbonate,  $\text{Fe}(\text{HCO}_3)_2$ , but that this compound is so unstable that it is known only in aq. soln. The relations between the ferrous carbonate and carbonated water are similar to those which obtain with the alkali and calcium carbonates. The conditions of equilibrium are represented by the five equations: (i),  $[\text{H}^+][\text{HCO}_3^-] = K_1[\text{H}_2\text{CO}_3]$ ; (ii),  $[\text{H}^+][\text{CO}_3^{--}] = K_2[\text{HCO}_3^-]$ ; (iii),  $[\text{Fe}^{++}][\text{CO}_3^{--}] = K_3$ , the **solubility product**; (iv),  $[\text{HCO}_3^-] = 2[\text{Fe}^{++}]$ ; and (v),  $\alpha[\text{Fe}(\text{HCO}_3)_2] = [\text{Fe}^{++}]$ , where  $\alpha$  represents the degree of ionization of ferrous hydrocarbonate. By extrapolation from J. Kendall's values for  $K_1$ , it follows that  $K_1 = 3.7 \times 10^{-7}$  at  $30^\circ$ ; C. A. Seyler and P. V. Lloyd's value for  $K_2 = 4.91 \times 10^{-11}$  at  $25^\circ$ . The following is a selection from H. J. Smith's solubility data for ferrous hydrocarbonate in water at  $30^\circ$ :

[H <sub>2</sub> CO <sub>3</sub> ]	0.1868	0.2168	0.3116	0.4046	0.6600	0.7154	0.7600
[Fe(HCO <sub>3</sub> ) <sub>2</sub> ]	0.00245	0.00262	0.00304	0.00332	0.00402	0.00418	0.00434
<i>a</i>	0.912	0.908	0.902	0.896	0.884	0.880	0.878
<i>K</i> × 10 <sup>3</sup>	3.91	3.96	4.04	4.02	4.08	4.11	4.18

The average of the whole series of determinations was  $K=4.04 \times 10^{-3}$ . It is therefore possible to calculate the value of  $K_3=[Fe^{++}][CO_3^{--}]$ , since  $K_3=4K_2K^3/K_1$ ; and this gives  $K_3=34.53 \times 10^{-12}$ . Consequently, if ferrous carbonate were not hydrolytically dissociated, its solubility in pure water free from carbon dioxide would be  $5.8 \times 10^{-6}$  mol. J. Tillmans and B. Klarmann calculated  $2.7 \times 10^{-10}$ , for the solubility product. L. A. Klyachareff studied the effect of ferric hydroxide on the solubility of carbon dioxide in water. W. Feitknecht found the space-lattice of **ferrous oxycarbonate**,  $FeCO_3 \cdot 3Fe(OH)_2$ , corresponds with alternate layers of hydroxide and normal salt.

J. W. Döbereiner showed that when ferrous carbonate is heated with **potassium hydroxide**, ferrosic oxide is formed and carbon monoxide is given off and potassium carbonate is formed. J. Lemberg said that boiling potash-lye blackens siderite but not so with calspar or dolomite; and R. Böttger found that with precipitated ferrous carbonate, a boiling soln. of potassium hydroxide forms ferrosic oxide. J. R. Baylis found that the solubility of precipitated ferrous carbonate, *S* parts of Fe per million, in water containing CO<sub>2</sub> parts per million in water sat. with **calcium hydroxide**, and with the H<sup>+</sup>-ion conc.  $p_H$  is:

CO <sub>2</sub>	9.7	7.9	5.3	8.8	0	0	0
$p_H$	7.0	7.3	7.5	7.4	8.6	8.6	8.6
<i>S</i>	4.0	2.0	0.8	2.5	trace	trace	0.10

E. Braun observed that ferrous carbonate is readily soluble in a soln. of **ammonium hydrocarbonate**, and rather less in soln. of **sodium and potassium hydrocarbonates**. H. Chandra found that a soln. of 120 grms. NaHCO<sub>3</sub> per litre can dissolve 0.828 grms. of Fe; a sat. soln. of potassium hydrocarbonate 0.908 gm. per litre. If the soln. in ammonium hydrocarbonate or in **rubidium hydrocarbonate** is oxidized in air, complex ferrosic salts are formed,  $[Fe_2''Fe(CO_3O)]'$ . O. Hauser obtained a colourless soln. of ferrous carbonate in one of **ammonium carbonate**. J. Ville found that the alkali or alkaline **earth carbonates** precipitate hydrated ferrous oxide from carbonated water holding ferrous carbonate in soln., and they are themselves converted into hydrocarbonates; hence the alkali and alkaline earth carbonates have no action on chalybeate water. J. R. Baylis found that with **calcium carbonate** and soln. containing CO<sub>2</sub> parts per million, the solubility of ferrous carbonate, *S* parts Fe per million, when the H<sup>+</sup>-ion conc. of the soln. is  $p_H$  is:

Time	2	4	6	29	26 days
CO <sub>2</sub>	3.5	2.6	1.8	5.3	6.6
$p_H$	7.3	7.4	7.4	7.3—	7.4—
<i>S</i>	1.6	1.3	0.8	1.8	0.6

H. Ehlert obtained the following results for the solubility of ferrous carbonate in water alone, and in water with carbon dioxide at 2 atm. press., containing *S* grms. of ferrous carbonate per litre, and also containing different proportions of the salts—**sodium and magnesium chlorides**, and of **sodium and magnesium sulphates**—indicated in square brackets expressed in terms of grams of salt per 1000 grms. of water, when *S* for water alone is 6.1907. The results with an asterisk refer to water free from carbon dioxide.

[NaCl]	351.2*	50	106.9	175.6	263.4	351.2
<i>S</i>	0.35042*	6.3541	5.7001	5.0226	4.3218	3.9246
[MgCl <sub>2</sub> ·6H <sub>2</sub> O]	2300.0*	86.9	700.0	1150.0	1725.0	2300.0
<i>S</i>	4.2049*	5.8403	4.5553	4.4587	5.3975	9.0524
[Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O]	137.7*	Sat. at 14°	137.7	Sat. at 14°	—	—
<i>S</i>	0.70085*	0.93444*	7.9428	9.5780	—	—
[MgSO <sub>4</sub> ·7H <sub>2</sub> O]	105.3*	Sat. at 18°	105.3	Sat. at 18°	—	—
<i>S</i>	1.4667*	2.9334*	6.2423	7.3922	—	—



F. Wöhler found that when siderite is heated in a current of **chlorine**, it yields a sublimate of ferric chloride and a residue of ferric oxide mixed with some ferrous chloride if the supply of chlorine is deficient:  $6\text{FeCO}_3 + 3\text{Cl}_2 = 2\text{FeCl}_3 + 2\text{Fe}_2\text{O}_3 + 6\text{CO}_2$ . W. Kangro and R. Flügge added that at  $900^\circ$ , 84.3 per cent. of iron was removed by chlorine from siderite in 120 mins. H. de Sénarmont said that crystalline ferrous carbonate, prepared at a high temp., is but slowly attacked by **acids**, and J. Durocher found that bubbling with the escape of carbon dioxide occurs only when the mixture is heated, but B. Bruzs observed that the artificial ferrous carbonate readily dissolves in acids. Siderite is slowly attacked by **hydrochloric acid** with the evolution of carbon dioxide.

J. J. Berzelius observed that when **hydrogen sulphide** is passed over ferrous carbonate at  $100^\circ$ , iron disulphide, sulphur dioxide, water, and hydrogen are formed. C. Doelter obtained crystals of pyrite by the action of water sat. with hydrogen sulphide on siderite in a sealed tube at  $80^\circ$  to  $90^\circ$ . W. P. Jorissen and J. Rutten found that the action of hydrogen sulphide on precipitated basic carbonate is more rapid than it is on normal ferrous carbonate. H. Lotz investigated the action of air with 19 per cent. of carbon dioxide and 1 per cent. of **sulphur dioxide** on moist siderite, and found that some iron and manganese oxides become soluble in water. A. Gorgeu found that molten **alkali sulphate** mixed with a little **alkali sulphite** reacts with siderite forming crystals of ferrosic oxide with inclusions of manganese, calcium, and magnesium ferrites. J. W. Döbereiner found that at a high temp. conc. **sulphuric acid** acts on powdered siderite forming carbon dioxide, then sulphur dioxide and ferrosic sulphate. According to V. Lenher and C. H. Kao, siderite does not react with **selenium dichloride**.

According to R. H. Brett, ferrous carbonate is insoluble in an aq. soln. of **ammonium chloride or nitrate**, but A. Terreil showed that it is soluble in a boiling soln. of an ammonium salt. G. Linck added that siderite is rapidly oxidized by a mixture of ammonium nitrate and sodium chloride at  $60^\circ$  to  $70^\circ$ . L. Cambi and co-workers found that **nitric oxide** gives with ferrous carbonate an unstable product which could not be isolated; and as the nitric oxide is reduced to nitrous oxide, some hyponitrite is formed. W. Dominik represented the action of **nitric acid** on a mush of ferrous carbonate by:  $3\text{FeCO}_3 + \text{HNO}_3 + 4\text{H}_2\text{O} = 3\text{Fe}(\text{OH})_3 + \text{NO} + 3\text{CO}_2$ . O. Baudisch and co-workers found that freshly-precipitated ferrous carbonate reduces **alkali nitrites and nitrates** to form ammonia.

H. C. Bolton observed that siderite is not attacked by a cold, sat. soln. of **oxalic acid**; likewise with cold, sat. soln. of **citric, tartaric, or acetic acid**, but if the soln. are hot, the carbonate is attacked. If moist precipitated ferrous carbonate be warmed with **sugar**, C. Klauer found that carbon dioxide is developed, and the ferrous oxide which is formed is protected from oxidation to some extent by the sugar. The reaction was studied by A. Buchner, R. Phillips, etc.—*vide supra*. W. Spiepermann found that the reaction with **alkali thiocyanate**,  $\text{KCys} + \text{FeCO}_3 = \text{KCyo} + \text{FeS} + \text{CO}_2$ , begins at  $280^\circ$ , and proceeds rapidly between  $280^\circ$  and  $340^\circ$ . A. Simon and T. Reetz studied the reaction with **benzidine chloride**. I. I. Wanin and A. A. Tschernojarowa found that at  $55^\circ$  to  $60^\circ$ , **benzylidene chloride** reacts turbulently with ferrous carbonate. W. H. Coghill and J. B. Clemmer discussed the **soap** flotation of siderite. H. le Chatelier represented the reaction with **silica** by:  $\text{FeCO}_3 + \text{SiO}_2 = \text{FeSiO}_3 + \text{CO}_2 - 7.6 \text{ Cals.}$

H. Rose observed that **ferric oxide** can drive the carbon dioxide from ferrous carbonate. A soln. of a **cuprous salt** in ammonium carbonate was found by E. Braun to be reduced by freshly-precipitated ferrous carbonate to form copper; T. S. Hunt made a similar observation with respect to **cupric chloride**; and H. C. Biddle observed that a precipitated mixture of cupric and ferrous carbonates forms copper and basic ferric carbonate. A. F. Rogers found that siderite reduces a soln. of **silver sulphate** to form silver. J. Ville found that ferrous carbonate is soluble in a soln. of a **ferric salt** with the evolution of carbon dioxide, and the precipitation of hydrated ferric oxide. A. Sismonda investigated the conversion of

siderite into limonite through the action of a soln. of **ferrous sulphate** formed by the weathering of pyrites.

The fact that ferrous carbonate is very sparingly soluble in water alone, but is soluble in water containing carbon dioxide in soln., is explained by analogy with the behaviour of calcium carbonate, by assuming that soluble **ferrous hydrocarbonate**,  $\text{Fe}(\text{HCO}_3)_2$ , is formed, although this salt has not yet been prepared in the solid state. O. Haehnel assumed that this salt will appear as a solid phase in soln. with carbon dioxide under a press. exceeding 40 atm.; and H. J. Smith calculated that the press. of carbon dioxide with solid ferrous hydrocarbonate at  $25^\circ$  is greater than 25 atm.

L. Gmelin stated that iron dissolves in an aq. soln. of carbon dioxide with the evolution of hydrogen. H. Klut also observed the evolution of hydrogen when water free from dissolved oxygen acts on iron. G. T. Moody showed that when iron is left for 26 days in contact with a soln. of carbon dioxide at atm. press., 1.66 grms. of iron per litre dissolve as ferrous hydrocarbonate; and J. Günzburg found that in the absence of oxygen, water sat. with carbon dioxide under atm. press. dissolves about a gram of iron per litre in a few days. The soln. of hydrocarbonate is stable if it be separated from the excess of iron, but if it be shaken with iron, with or without the introduction of more carbon dioxide, white ferrous carbonate is formed. E. Müller and H. Henecka found that with the carbon dioxide under a press. of 50 atm., water with pulverulent iron in suspension at  $30^\circ$  to  $100^\circ$  attains a maximum concentration of hydrocarbonate, and this the more rapidly the higher the temp. The concentration of the hydrocarbonate in soln. then decreases owing to its decomposition into ferrous carbonate, etc. At  $20^\circ$ , a concentration of 2.249 grms. of iron per litre is attained, but, as shown in Fig. 681, the maximum is less pronounced at  $20^\circ$  to  $60^\circ$  than it is at  $80^\circ$  to  $100^\circ$ . The decrease in the concentration of the hydrocarbonate after attaining a maximum was also observed by N. N. Gavriloff and co-workers. The observations of J. Kendall, C. A. Seyler and P. V. Lloyd, H. J. Smith, and J. Tillmans and B. Klarmann have just been discussed.

M. Golfier-Besseyre prepared a soln. of the hydrocarbonate by passing carbon dioxide into a flask filled with water and iron turnings, and M. Sarzeau said that the reaction is accelerated if pieces of platinum wire are also present. The formation of a soln. of hydrocarbonate by the action of a soln. of carbonic acid on iron was observed by A. C. Brown, H. Bunte and A. Schmidt, F. C. Calvert, W. R. Dunstan and co-workers, J. Günzburg, C. von Hauer, B. Klarmann, W. Leybold, A. Simon and K. Kötschau, L. N. Vauquelin, and J. Ville. According to G. Stadnikoff and N. Gavriloff, the dissolution of iron is faster if the carbon dioxide be passed through the water in the presence of iron than if the water be first sat. with carbon dioxide; and the rate of dissolution increases the faster the current of gas. Rusty iron dissolves more quickly than clear iron; iron etched with hydrochloric acid dissolves more rapidly than the untreated iron; iron previously used for the preparation of the hydrocarbonate dissolves less quickly than ordinary iron. If air be present so that the ratio  $\text{CO}_2 : \text{Air} = 1 : 1$ , the rate of dissolution of iron is independent of time; if the ratio is  $1 : 3$ , the rate of dissolution is still independent of time, but it is less than when the ratio is  $1 : 1$ , since part of the iron goes into oxide. N. N. Gavriloff and co-workers found that if over 5 per cent. of oxygen and 14 to 15 per cent. of carbon dioxide are present in flue-gases, the velocity of formation of the hydrocarbonate is retarded owing to the formation

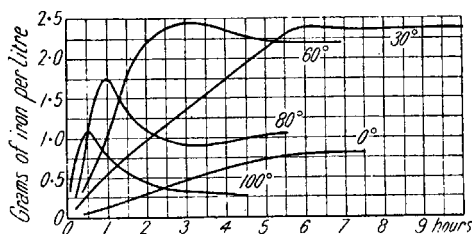


FIG. 681.—Solubility of Iron in Water Carbonated at 50 atm. Pressure.

of a layer of oxide on the metal. A. Simon and K. Kötschau found that by triturating ferrum reductum in a porcelain mortar, in the presence of carbon dioxide and moisture, some ferrous hydrocarbonate is formed. F. Haber and F. Goldschmidt said that some hydrocarbonate is formed with iron as anode in an aq. soln. of carbon dioxide with a current of 0.005 amp. per sq. cm.

L. Gmelin, A. Buchner, and G. Just obtained a soln. of the hydrocarbonate by the action of carbonated water on precipitated ferrous carbonate. C. Peeters said that the hydrocarbonate is precipitated by mixing aq. soln. sat. with carbon dioxide containing respectively a ferrous salt and an equimolar proportion of an alkali hydrocarbonate together with 1 to 5 per cent. of an alkali tartrate, citrate, lactate, etc. W. Leybold found that precipitated ferrous hydroxide dissolves in carbonated water more slowly than iron. N. N. Gavriloff and S. K. and P. K. Mel discussed the formation of the hydrocarbonate from carbon dioxide and iron oxide. F. K. Cameron and W. O. Robinson measured the vap. press.,  $p$  cm., of carbon dioxide over moist hydrated ferrous oxide (0.1231 grm. FeO), and found, for added carbon dioxide :

[CO <sub>2</sub> ].	0.0	0.014	0.070	0.098	0.126	0.182	0.224	0.252 grm.
$p$	76	76	76	102	134	199	245	274 cm.

The break in the curve, Fig. 682, represents the point where all the ferrous oxide has been converted into normal carbonate. The result is taken to show that with vap. press. less than 4.5 atm. of carbon dioxide, no other than the normal carbonate, or a hydrate of the normal carbonate, can exist as a solid phase. W. Thörner said that some hydrocarbonate is formed when carbonated water acts on pyrite:  $\text{FeS}_2 + 2\text{CO}_2 + 2\text{H}_2\text{O} = \text{Fe}(\text{HCO}_3)_2 + \text{S} + \text{H}_2\text{S}$ .

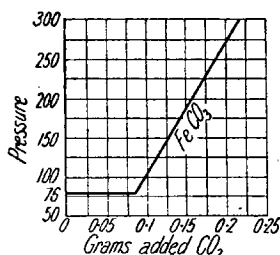


FIG. 682.—The Adsorption of Carbon Dioxide by Hydrated Ferrous Oxide.

H. Molisch observed that light does not accelerate the oxidation of ferrous hydrocarbonate to ferric hydroxide; and in the absence of air, A. Simon and K. Kötschau found that the soln. is not decomposed by ultra-violet light; E. C. C. Baly observed the formation of carbohydrates when a soln. of the hydrocarbonate is exposed to ultra-violet light.

O. Baudisch and D. Davidson found that when the soln. is exposed to the light of a carbon arc, hydrogen is evolved, and the ferrous hydrocarbonate is oxidized. O. Haehnel found the electrical conductivity of aq. soln. at 18° to be :

FeCO <sub>3</sub>	0.077	0.072	0.01	0.005 per cent.
Mho $\times 10^{-6}$	369	349	195	96

Measurements were also made by J. Günzburg, who found that the transport number of the Fe<sup>++</sup>-ion is independent of the age of the soln., and amounts to about 0.5. The colourless soln. of ferrous hydrocarbonate—called *steel-water*, or *chalybeate water*—has a slightly ferruginous taste, and L. Gmelin observed that when the soln. is exposed to air, hydrated ferric oxide is precipitated and carbon dioxide is evolved. If the excess of carbon dioxide is expelled from the soln. without the entry of air, M. Golfer-Besseyre found that white ferrous carbonate is precipitated; and A. C. Brown, that in an atm. free from oxygen and carbon dioxide, gas is evolved and ferrous carbonate is precipitated, but in the presence of oxygen, some ferric hydroxide is formed. If the aq. soln. be boiled in a flask with a reflux condenser, all the carbon dioxide is expelled, and, according to W. R. Whitney, colloidal ferric oxide is formed. In the absence of air, the soln. remains clear and colourless, but G. T. Moody found that when the soln. is boiled, green ferrous carbonate is precipitated, and it becomes reddish-brown in air; atm. oxygen decomposes the soln. precipitating ferrous and ferric hydroxides, and ferrous carbonate.

J. Ville noted that the presence of chlorides and sulphates retard the decomposition of chalybeate water by aerial oxidation; and the presence of sugar, or glycerol, was found by C. Klauer, G. Bischof, R. Phillips, etc.—*vide supra*—to make the soln. a little more stable in air. L. N. Vauquelin observed that with hydrogen sulphide, the soln. does not give a precipitate of black iron sulphide until the liquid has been exposed to the air for some time; the sulphide is formed as the carbon dioxide escapes. C. H. Pfaff added that whilst tincture of galls gives no coloration or precipitate with ferrous salts in the absence of all traces of ferric salts, a purple coloration or precipitate is produced with a soln. of ferrous hydrocarbonate. L. Cambi and A. Clerici found that nitric oxide forms an unstable product when it acts on a soln. of ferrous hydrocarbonate.

**Complex ferrous carbonates.**—O. Hauser also obtained a colourless soln. of ferrous carbonate in one of ammonium carbonate; presumably **ammonium ferrous carbonate** is formed. According to W. C. Reynolds, **potassium ferrous carbonate**,  $K_2CO_3 \cdot FeCO_3 \cdot 4H_2O$ , is produced by mixing, out of contact with air, a conc. soln. of ferrous chloride mixed with an excess of potassium carbonate. The white precipitate first formed soon dissolves producing a greenish soln. which deposits white, scaly crystals of the double salt.

A. Breithaupt described a mineral from Traversella, Piedmont, which he called *Mesitenspath* or *mesitine*, and this was later modified to **mesitite**—from *μεσίτης*, a go-between—in allusion to its being intermediate between magnesite and siderite. The analysis approximates magnesium ferrous tricarbonates,  $2MgCO_3 \cdot FeCO_3$ . He afterwards obtained a similar mineral from the same locality, and from Thurnberg, Saxony, and he called it **pistomesite**—from *πιστός*, reliable, and *μεσίτης*, a go-between—because pistomesite is nearer the middle between siderite and magnesite than mesitite, being **magnesium ferrous carbonate**,  $MgCO_3 \cdot FeCO_3$ . Analyses were reported by O. W. Gibbs, J. Fritsche, A. Patera, and C. Ettling. Probably both are stages in a series of solid soln.—*vide supra*. The colour of the minerals is yellowish-white, yellowish-grey, or yellowish-brown; and the crystals are rhombohedral. The (10 $\bar{1}$ 1)-cleavage is perfect. The sp. gr. of mesitite is 3.35 to 3.36, and of pistomesite, 3.42. The hardness is 3.5 to 4.0. There are also F. Sandberger's **ferrobrucite**,  $(Mg, Fe)O \cdot CO_2 \cdot 10H_2O$ , discussed by P. Gaubert; *breunerite* is  $3FeCO_3 \cdot 8MgCO_3$  approximately; V. Zsivny's  $(Fe, Mg, Ca)CO_3$ , where Fe : Mg : Ca = 1 : 49 : 50—*vide ankerite*, 4, 29, 367; and E. Artini's pink, micaceous mineral, **brugnatellite**, found in the Val Malenco, Lombardy, and also on the Monte Ramazzo, Luguria, which approximates  $MgCO_3 \cdot 5Mg(OH)_2 \cdot Fe(OH)_3 \cdot 4H_2O$ . It is uniaxial with a perfect cleavage, and a refractive index of 1.533 with Na-light; the optical character is negative. It is pleochroic being  $\omega$ =yellowish-red, and  $\epsilon$ =colourless. R. L. Codazzi found an ash-brown complex carbonate,  $(Ca, Mg, Fe, Ce)CO_3$ , in Muzo, Coscuez, and Coper, Colombia, and named it **codazzite**—after A. Codazzi. It belongs to the rhombohedral system; its sp. gr. is 2.5, and its hardness, 4.

Solid soln. of manganous and ferrous carbonates occur in nature as *rhodochrosite-siderite*, or *manganosiderite* reported by A. Breithaupt, who called the mineral **oligonite**. It was called *manganosphärite* by K. Busz, but E. B. Mayo and W. J. O'Leary, W. E. Ford, E. H. Kraus and W. F. Hunt, S. Koch and L. Zombory, and N. H. and A. N. Winchell preferred oligonite. The optical properties were studied by N. Sundius, E. T. Wherry and E. S. Larsen, G. F. Loughlin, W. E. Ford, and E. B. Mayo and W. J. O'Leary.

**Ferric carbonates.**—According to L. Gmelin, the precipitate obtained by adding potassium carbonate to a soln. of ferric nitrate, when thoroughly washed, is hydrated ferric oxide free from carbon dioxide; and E. Soubeiran found that the precipitate obtained from ferrous salts under like conditions, when exposed in a thin layer to moist air in a cellar for six months, contains about 8.3 per cent. of carbon dioxide, 20 per cent. of water, and 71.4 per cent. of ferric oxide—no ferrous iron was present. W. Scheermesser, R. Rother, K. Seubert and M. Elten, A. Langlois,

J. Lefort, W. Wallace, J. Barratt, and T. Parkman obtained similar results by precipitating soln. of ferric salts with alkali or ammonium carbonates. The ratios  $\text{Fe}_2\text{O}_3 : \text{CO}_2 : \text{H}_2\text{O}$  ranged from 9 : 1 : 12 to mixtures with only 1.36 per cent. carbon dioxide. K. Feist triturated crystals of ferric chloride with a slight excess of hydrated sodium carbonate, and when carbon dioxide was no longer evolved, the liquid mixture was treated with water and the precipitate allowed to settle. When dried, a precipitate 7 : 1 : 8 was obtained. The composition varied with the time of washing, showing that the treatment with water induced hydrolysis.

Taking the mol. ratios  $\text{Fe}_2\text{O}_3 : \text{CO}_2 : \text{H}_2\text{O}$ , the following basic salts have been reported : 3 : 1 : 6 and 9 : 1 : 12, by W. Wallace ; 3 : 1 : 8, by J. Barratt ; 3 : 1 : 4, by W. Wallace, and J. Barratt ; 1 : 1 :  $n$ , by T. Parkman ; 6 : 3 : 12, by R. Rother ; and 10 : 1 : 28, by K. Seubert and M. Elten.

All this shows that if **ferric carbonate**,  $\text{Fe}_2(\text{CO}_3)_3$ , is formed, it is immediately hydrolyzed in aq. soln. P. N. Raikow observed that carbon dioxide acting on freshly-precipitated ferric oxide forms no ferric carbonate. J. Tillmans and co-workers found that precipitated hydrated ferric oxide adsorbs carbon dioxide from the soln., and the results with a fresh preparation did not differ from those with one 8 days old ; a precipitate obtained from a hot soln. adsorbed less than one from a cold soln. When the amount of precipitant, sodium hydrocarbonate, is constant, the amount of adsorbed carbon dioxide increases with the conc. of that gas in the soln. ; and when the amount of carbon dioxide is kept constant, the amount of carbon dioxide adsorbed increases with the conc. of sodium hydrocarbonate. It is assumed that the adsorption is attended by the formation of **ferric hydroxycarbonate**,  $\text{Fe}(\text{OH})\text{CO}_3 \cdot n\text{Fe}(\text{OH})_3$ . F. K. Cameron and W. O. Robinson found the vap. press.,  $p$  cm., of carbon dioxide over wet ferric hydroxide at  $0^\circ$  in the presence of the number of grams of carbon dioxide indicated by the square brackets :

$[\text{CO}_2]$ . . .	0	0.014	0.070	0.140	0.182	0.224	0.256 grm.
$p$ . . .	76	85	148	224	273	318	368 cms.

The whole of the results fall on a straight line, and show practically no adsorption, and this is in agreement with the observations of P. N. Raikow. A. Gatterer observed that the hydrosol of ferric hydroxide absorbs 20 per cent. more carbon dioxide than does the carbonate alone ; consequently, he inferred that a complex ferric carbonate is formed. The subject was studied by A. von Dobeneck, and E. Reichardt and E. Blumtritt—*vide* hydrated ferric oxide.

According to O. Hauser, the precipitates formed by adding ammonium carbonate to soln. of ferrous or of ferric salts are soluble in an excess of the precipitant. The ferric salt furnishes a blood-red liquid from which the iron is precipitated by hydrogen sulphide, by reagents which react with carbonates, or by boiling alkali-lye, but not by potassium ferrocyanide ; whereas prussian blue dissolves in an aq. soln. of ammonium carbonate to form a violet-red soln. It is therefore assumed that the liquid contains **ammonium ferric carbonate**, and it can be preserved in a closed vessel for several weeks, but deposits hydrated ferric oxide on evaporation.

J. Lefort could not prepare a definite **ferrosic carbonate**, although the partially-oxidized precipitate formed when an alkali carbonate is added to a soln. of a ferrous salt, may contain both ferrous and ferric carbonates or oxycarbonates. The white precipitate obtained with ferrous salts is less readily dissolved by an excess of ammonium carbonate, and the colourless soln., on treatment with hydrogen dioxide, or on exposure to air, rapidly turns brown ; but when oxidized by a limited quantity of air, it deposits **ammonium ferrous ferric oxycarbonate**,  $\text{NH}_4\text{CO}_3 \cdot \text{FeCO}_3 \cdot \text{FeCO}_3 \cdot \text{FeO} \cdot 2\text{H}_2\text{O}$ , in the form of stellate aggregates of small, doubly-refracting, green prisms. When the crystals are exposed to air, they become olive-green, and finally brown, owing to the formation of hydrated ferric oxide. The salt dissolves in dil. acids, with evolution of carbon dioxide, to form a yellowish-green soln., and when treated with alkali hydroxides, it yields

ammonia, and black, strongly magnetic, ferrosic oxide. R. Frey and J. Burghelle described a pink, pleochroic, basic carbonate,  $2\text{Fe}_2\text{O}_3 \cdot \text{Cr}_2\text{O}_3 \cdot 27\text{MgO} \cdot 0.6\text{CO}_2 \cdot 54\text{H}_2\text{O}$ , from Bou Oufroh, in Morocco. The sp. gr. is 2.1 to 2.2; and the hardness, 1.

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### § 49. The Iron Nitrates

H. Davy<sup>1</sup> showed that when conc. nitric acid acts upon iron, nitric oxide is given off with great rapidity, and a great rise of temp.; the soln. assumes a yellow tint, and as the process goes on, a yellow oxide is precipitated. The soln. was assumed to contain **ferric nitrate**,  $\text{Fe}(\text{NO}_3)_3$ , because it gives a red precipitate with alkalies, and a bright blue precipitate with potassium ferrocyanide. On the other hand, with very dil. nitric acid, say of sp. gr. 1.16, the iron dissolves without the assistance of heat, and without the evolution of gas for some time, and the soln. becomes dark olive-brown. The liquid was assumed to contain **ferrous nitrate**,  $\text{Fe}(\text{NO}_3)_2$ , because it gives a pale green precipitate with alkalies, and a pale green coloration with potassium ferrocyanide. Iron thus forms two nitrates as well as two sulphates, two chlorides, etc. The existence of the green nitrate was not suspected by J. L. Proust. H. Davy said that he had not succeeded in preparing ferrous nitrate which gave only a white precipitate with potassium ferrocyanide, that is, a soln. which contained only iron "at its minimum oxidation"; for when

pure, green iron oxide is dissolved by very dil. nitric acid, a small quantity of the acid is generally decomposed, which is likewise the case when potassium nitrate is decomposed by ferrous sulphate. A soln. is said to be obtained by treating ferrous sulphate with an eq. quantity of barium nitrate, and evaporating the filtrate in vacuo over sulphuric acid.

A. Scheurer-Kestner observed that with nitric acid of sp. gr. 1.034, ferrous and ammonium nitrates are formed; with acid of sp. gr. 1.073, ferrous, ferric, and ammonium nitrates; with acid of sp. gr. 1.115, ferric nitrate alone; and with acid of sp. gr. over 1.115, ferric and basic ferric nitrates are produced. The subject was investigated by W. Heldt. According to J. M. Ordway, the progress of the reaction depends on the temp. as well as on the conc. of the acid, and it is also affected by the nature of the impurities—*e.g.*, sulphur and phosphorus—in iron. With nitric acid of sp. gr. 1.05, iron of a high degree of purity furnishes ferrous nitrate, but more conc. acids, a mixture of ferrous and ferric nitrates is produced. C. Montemartini observed that ferrous nitrate is first formed even with conc. acids, but it is then oxidized to ferric nitrate by the nitrogen oxides simultaneously formed. N. A. E. Millon found that the presence of platinum chloride influences the formation of the ferric salt, and A. Quartaroli made a similar observation with respect to urea. The formation of iron nitrates and nitrites in hydrated ferric oxide, or in iron-rust, which has been exposed to the air for a long time, was discussed by A. Baumann, E. Donath, and H. Ditz and co-workers. F. W. Bergstrom noted that the salt is formed by the action of a soln. of ammonium nitrate in liquid ammonia on iron wire.

**The preparation of ferrous nitrate.**—J. J. Berzelius said that in preparing a soln. of ferrous nitrate by dissolving iron in nitric acid, the iron should be immersed in water, and nitric acid, free from nitrous acid and chlorine, should be added in small portions, with constant agitation, so that the temp. may not rise above 50°; as often as the liquid cools down, fresh acid should be added. Under these circumstances no gas is evolved, but some ammonium nitrate is formed:  $4\text{Fe} + 10\text{HNO}_3 = 4\text{Fe}(\text{NO}_3)_2 + \text{NH}_4\text{NO}_3 + 3\text{H}_2\text{O}$ . A. Pleischl found that with a mixture of 1 part of acid with 3 of water, a mixture of nitric and nitrous oxides is at first evolved, and afterwards only nitric oxide. J. J. Berzelius also noted that ferrous sulphide and well-cooled nitric acid forms a soln. of ferrous nitrate and gives off hydrogen sulphide. If the temp. is allowed to rise, some ferric salt is formed. J. M. Ordway also dissolved ferrous sulphide in well-cooled nitric acid of sp. gr. less than 1.12, and evaporated the soln., as nearly as possible, at 60°. C. F. Schönbein regarded the crystals obtained from a soln. of the scale-oxide of iron in conc. nitric acid as ferric nitrate; L. N. Vauquelin, as ferrous nitrate which is converted into ferric nitrate and a yellow deposit on exposure to air. I. Traube, and A. A. Noyes and B. F. Brann obtained an aq. soln. by the action of barium nitrate on a soln. of ferrous sulphate, and filtering off the precipitated barium sulphate; R. Funk said that the soln. so obtained are very dilute, and are particularly prone to oxidation on evaporation, and he recommended triturating solid lead nitrate with an equivalent proportion of hydrated ferrous sulphate along with some dilute alcohol, and afterwards evaporating the soln. E. Weitz and H. Müller recommended triturating the salts first with a little water, adding a few drops of soda-lye to avoid the effect of free acids, adding an equal vol. of alcohol, and evaporating the filtered soln. in air. A. A. Noyes and B. F. Brann reduced a soln. of ferric nitrate with silver:  $\text{Fe}(\text{NO}_3)_3 + \text{Ag} \rightleftharpoons \text{AgNO}_3 + \text{Fe}(\text{NO}_3)_2$ ; and W. H. Ross, and O. Baudisch and E. Mayer found that ferrous nitrate is formed when a soln. of ferric nitrate is exposed to sunlight, or to ultra-violet light; but M. Schneider observed no reduction in sunlight.

Anhydrous ferrous nitrate has not been prepared; when the aq. soln. is evaporated, green, monoclinic prisms of the *hexahydrate*,  $\text{Fe}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , are formed. J. M. Ordway found that 100 parts of water dissolve 200 parts of the crystals at 0°; 245 parts at 15°; and 300 parts at 25°. R. Funk and F. Mylius obtained rather

larger values, and their results, summarized in Fig. 683, are as follow, when the solubility,  $S$ , refers to grams of  $\text{Fe}(\text{NO}_3)_2$  in grams of soln. :

	-145.5°	-20°	-28°	-27°	-19°	-12°	-10°	0°	20°	60.5°
$S$	29.8	32.8	35.5	35.6	36.5	39.4	39.6	41.5	45.5	62.5
	Ice		$\text{Fe}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$				$\text{Fe}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$			

While the hexahydrate separates from conc. soln. when the temp. is between  $-12^\circ$  and  $60.5^\circ$ , the *enneahydrate*,  $\text{Fe}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ , separates when the temp. is between  $-12^\circ$  and  $-28^\circ$ . A. Gorboff concluded from insufficient evidence that there is an *octodecahydrate*,  $\text{Fe}(\text{NO}_3)_2 \cdot 18\text{H}_2\text{O}$ , and a *pentadecahydrate*,  $\text{Fe}(\text{NO}_3)_2 \cdot 15\text{H}_2\text{O}$ . H. C. Jones and H. P. Bassett discussed the relation between the temp. of crystallization, and the number of mols. of water of crystallization of the salt.

**The physical properties of ferrous nitrate.**—R. Funk said that the hexahydrate furnishes pale green, rhombic plates. J. M. Ordway found that soln. sat. at  $0^\circ$ ,  $15^\circ$ , and  $25^\circ$  have respectively the sp. gr. 1.44, 1.48, and 1.50. R. Funk observed that the soln. sat. at  $18^\circ$  has a sp. gr. 1.497; and I. Traube, that soln. with 4.554 and 6.052 per cent.  $\text{Fe}(\text{NO}_3)_2$  have the respective sp. gr. 1.03556 and 1.04835. I. Traube discussed the mol. soln. vol. R. Funk said that the hexahydrate melts at  $60.5^\circ$ . The molten salt was found by R. Funk to decompose with the evolution of a gas if heated a little above the m.p.; a dark red residue remains. According to C. Montemartini and E. Vernazza, the decomposition of ferrous nitrate by heat is represented by:  $2\text{Fe}(\text{NO}_3)_2 = 2\text{FeO} + 4\text{NO}_2 + \text{O}_2$ ; but since the ferrous oxide is oxidized, and the water of crystallization is always present up to  $100^\circ$ , the resultant reaction is symbolized:  $3\text{Fe}(\text{NO}_3)_2 + 7\text{H}_2\text{O} \rightarrow 3\text{Fe}(\text{OH})_3 + 5\text{HNO}_3 + \text{NO}$ . The ferric oxide is present as  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ . The heat of formation was studied by P. A. Favre and J. T. Silbermann; M. Berthelot gave:  $(\text{Fe}, \text{N}_{2\text{gas}}, 3\text{O}_{2\text{gas}}, \text{Aq.}) = 119.0$  Cals.; and J. Thomsen,  $(\text{Fe}, \text{O}_{\text{gas}}, \text{N}_{2\text{O}_{5\text{gas}}}, \text{Aq.}) = 89.67$  Cals.; J. Thomsen also gave for the heat of neutralization:  $\text{Fe}(\text{OH})_2 + 2\text{HNO}_3 \cdot \text{Aq.} = \text{Fe}(\text{NO}_3)_2 \cdot \text{Aq.} + 21.339$  Cals., and M. Berthelot, 21.5 Cals.

F. Allison and E. J. Murphy studied the magneto-optic properties; H. M. Vernon, the change in the colour of aq. soln. on dilution or on raising the temp.; and S. Jakubsohn and M. Rabinowitsch, the electrical conductivity of the soln. H. Buff observed that in the electrolysis of dil. soln. of ferrous nitrate, iron and hydrated ferric oxide are formed; and J. H. Paterson said that between platinum electrodes, either iron, or with a small concentration and low current density, ferrous hydroxide is deposited. A. Schükareff found that when the electrolysis is conducted between platinum electrodes, in a magnetic field, a magnetochemical effect appears. G. Wiedemann made some observations on the magnetic susceptibility of the soln.

**The chemical properties of ferrous nitrate.**—J. M. Ordway reported that the crystals of the hexahydrate are stable in the cold, but the crystals, freed from the mother-liquor, rapidly form dark red basic ferric nitrate. R. Funk added that at ordinary temp. the crystals cannot be kept a day or two without browning, but at  $0^\circ$  they are stable. The crystals darken in a few minutes if traces of impurities, like hyponitrous acid, are present. J. J. Berzelius showed that the neutral aq. soln. decomposes when heated forming a basic ferric nitrate. J. M. Ordway added that the neutral soln. of ferrous nitrate, not too concentrated, can be boiled without decomposition, but if free acid is present, nitric oxide is evolved. R. Funk found that it is not possible to evaporate the soln. without some oxidation. W. Feitknecht observed that the space-lattice of **ferrous oxynitrate**,  $\text{Fe}(\text{NO}_3)_2$ ,

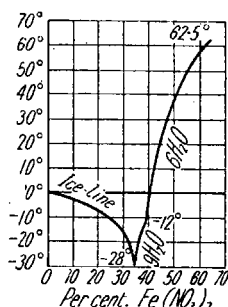


FIG. 683.—The Solubility of Ferrous Nitrate.

$4\text{Fe}(\text{OH})_2$ , corresponds with alternate layers of the normal salt and of the hydroxide.

J. Thomsen said that the thermal value of the reaction between ferrous nitrate and hydrogen sulphide, all in aq. soln., is  $-6.77$  Cals., and added that the negative value explains how hydrogen sulphide does not precipitate the sulphide from a soln. of ferrous nitrate. F. Haber electrolyzed a soln. of ammonium nitrate, sat. at  $0^\circ$ , between an iron cathode and a carbon anode, in a diaphragm cell, with a current density of  $0.02$  amp. per sq. dm., and obtained a golden-yellow liquid which, according to A. Kaufmann, contains an ammine of ferrous nitrate. He also said that a similar liquid is produced when powdered iron is digested with a hot, conc., ammoniacal soln. of ammonium nitrate. Observations were also made by W. Vaubel; E. Weitz and H. Müller said that the golden-yellow colour is due to the presence of complex nitrites, and added that **ferrous hexamminonitrate**,  $\text{Fe}(\text{NH}_3)_6(\text{NO}_3)_2$ , is formed by passing ammonia into a cold soln. of  $5$  grms. each of hexahydrated ferrous and ammonium nitrates in  $20$  c.c. of water from which air has been displaced by hydrogen. When the ferrous hydroxide first precipitated has dissolved, the liquid is filtered from the hydrated ferric oxide in an atm. of ammonia, and again treated with ammonia gas until a precipitate is formed. The precipitate is washed with ammoniacal alcohol, and then with dry ether, free from peroxide. The yellow tinge of the green, octahedral crystals is attributed to the presence of some colloidal ferric hydroxide. F. W. Bergstrom noted that the hexammine is formed in liquid ammonia. According to E. Weitz and H. Müller, if the filtered liquid from the hydrated ferric oxide be treated with nitric oxide, a mixture of crystals of the hexammine with black octahedra of **ferrous nitrosyl-pentamminonitrate**,  $[\text{Fe}(\text{NO})(\text{NH}_3)_5](\text{NO}_3)_2$ , is formed. The salt oxidizes in air with the evolution of ammonia, and it gives off nitric oxide when treated with acids. H. Davy observed that the soln. readily absorbs nitric oxide, and when the sat. soln. is heated, gas is liberated, and hydrated ferric oxide is precipitated. E. Weitz and H. Müller assumed that a **ferrous nitrosylpentaquonitrate**,  $[\text{Fe}(\text{NO})(\text{H}_2\text{O})_5](\text{NO}_3)_2$ , is formed.

W. Schrenzlowa found that **cuprous and ferrous nitrates** form isodimorphous solid soln. D. Vitali found that silver oxide decomposes the nitrate completely with the separation of ferrous hydroxide. M. V. Dover studied the reaction:  $\text{AgNO}_3 + \text{Fe}(\text{NO}_3)_2 \rightleftharpoons \text{Fe}(\text{NO}_3)_3 + \text{Ag}$ , and A. A. Noyes and B. F. Brann gave  $172.3$  Cals. for the thermal value of the reaction in soln. L. Losana observed that with finely-divided barium ferrate suspended in water, ferrous ferrate is formed. J. Jettmar discussed the action of the nitrate on animal skins in the tanning industry. E. H. Kraus reported that he prepared **didymium ferrous dodecanitrate**,  $2\text{Di}(\text{NO}_3)_3 \cdot 3\text{Fe}(\text{NO}_3)_2 \cdot 24\text{H}_2\text{O}$ , but could not repeat the result. The crystals were trigonal with the axial ratio  $a:c=1:5590$ , and  $\alpha=80^\circ 8'$ ; the (100)-cleavage distinct; the optical character negative; the birefringence strong; and the sp. gr. was  $2.257$ .

As indicated above, H. Davy<sup>2</sup> observed that if iron be dissolved in conc. nitric acid, **ferric nitrate**,  $\text{Fe}(\text{NO}_3)_3$ , is produced. If the acid be in excess, a brown soln. is formed, and if the acid be not in excess, a yellowish-brown basic salt is produced. The observations of A. Scheurer-Kestner, indicated above, showed that with nitric acid of sp. gr.  $1.115$ , ferric nitrate alone is formed; with a more dilute acid, ferrous nitrate appears, and with a more conc. acid, a basic ferric nitrate is formed. J. M. Ordway's observations are also discussed in connection with ferrous nitrate. W. Heldt proposed the hypothesis that the white skin formed on iron is anhydrous ferric nitrate and that it protects the iron from attack—*vide supra*, passivity—and he further assumed that the anhydrous salt so formed is insoluble in nitric acid of sp. gr.  $1.45$  to  $1.54$ . Otherwise, the anhydrous salt has not been isolated.

U. Antony and G. Gigli prepared the salt by adding the calculated quantity of nitric acid to a soln. of the basic nitrate, and this gives a neutral soln., but evaporating the soln. in vacuo over sulphuric acid does not furnish crystals. The

crystallization of the soln. is possible only in the presence of an excess of nitric acid. B. Lambert and J. C. Thomson electrolyzed a soln. of purified ferric chloride between iridium electrodes, and dissolved the electrodeposited iron in purified, dil. nitric acid. The soln. was concentrated on a water-bath, and re-crystallized several times from its soln. in conc. nitric acid. T. W. Richards and co-workers, G. P. Baxter and C. R. Hover, and F. K. Bell and W. A. Patrick described the preparation of the salt of a high degree of purity.

M. Z. Jovitschitsch prepared a soln. by passing nitrogen peroxide through a tower packed with pieces of glass, and finely-divided ferric oxide, and down which water trickled. C. Méne described the technical preparation of the salt by the action of nitric acid on iron slags; and G. Kingsley, by the action of nitric acid on pyrites.

**The hydrates of ferric nitrate.**—The equilibrium relations of the system  $\text{Fe}_2\text{O}_3\text{-N}_2\text{O}_5\text{-H}_2\text{O}$ , at  $25^\circ$ , were partially worked out by F. K. Cameron and W. O. Robinson. They observed as solid phases with soln. containing the percentage proportions  $\text{Fe}_2\text{O}_3 : \text{N}_2\text{O}_5$ : (i) ferric hydrotetranitrate,  $\text{Fe}_2\text{O}_3 \cdot 4\text{N}_2\text{O}_5 \cdot 18\text{H}_2\text{O}$ , with 3.25 to 3.93 : 49.6 to 47.2; (ii) enneahydrated ferric nitrate,  $\text{Fe}_2\text{O}_3 \cdot \text{N}_2\text{O}_5 \cdot 18\text{H}_2\text{O}$ , with 4.49 to 15.22 : 55.2 to 30.5—G. Malquori gave 5.99 : 45.84; (iii) G. Malquori gave for the transition point of the enneahydrate to the hexahydrate 9.25 : 46.48; (iv) hexahydrated ferric nitrate,  $\text{Fe}_2\text{O}_3 \cdot 3\text{N}_2\text{O}_5 \cdot 12\text{H}_2\text{O}$ , 9.28 : 48.88; and (v) F. K. Cameron and W. O. Robinson found the so-called basic ferric nitrates appear with 15.40 to 1.78 : 29.52 to 2.21. The following is a selection from F. K. Cameron and W. O. Robinson's results:

Sp. gr.	1.032	1.127	1.498	1.496	1.404	1.465	1.407	1.419
$\text{Fe}_2\text{O}_3$	1.78	5.79	15.40	15.22	5.02	4.49	3.93	3.52
$\text{N}_2\text{O}_5$	2.21	9.00	29.52	30.50	47.50	55.2	47.2	49.6
	Solid solution			$\text{Fe}_2\text{O}_3 \cdot 3\text{N}_2\text{O}_5 \cdot 18\text{H}_2\text{O}$			$\text{Fe}_2\text{O}_3 \cdot 4\text{N}_2\text{O}_5 \cdot 18\text{H}_2\text{O}$	

The results are plotted in Fig. 684. No definite basic salts are formed at  $25^\circ$ . The so-called basic salts are solid soln. of the three components,  $\text{Fe}_2\text{O}_3 \cdot m\text{N}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ ,

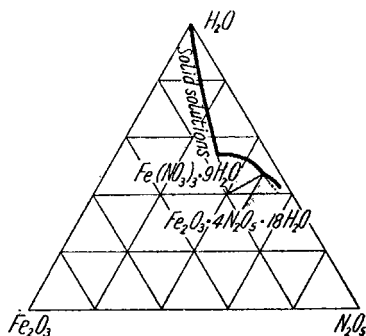


FIG. 684.—The Ternary System :  $\text{Fe}_2\text{O}_3\text{-N}_2\text{O}_5\text{-H}_2\text{O}$ , at  $25^\circ$ .

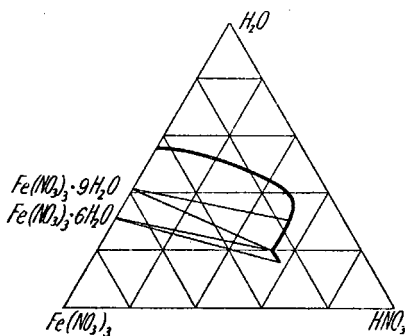


FIG. 685.—The Ternary System :  $\text{Fe}(\text{NO}_3)_3\text{-HNO}_3\text{-H}_2\text{O}$ , at  $25^\circ$ .

for the lines joining the points representing the composition of the liquid and the corresponding solid phase do not meet at a common point or points. When nitric acid is in excess, the lines do meet at a point corresponding with the enneahydrate. There is also an acidic nitrate, **ferric hydrotetranitrate**,  $\text{Fe}(\text{NO}_3)_3 \cdot \text{HNO}_3 \cdot 8\frac{1}{2}\text{H}_2\text{O}$ , which is less soluble than the normal nitrate. G. Malquori's study of the ternary system:  $\text{Fe}(\text{NO}_3)_3\text{-HNO}_3\text{-H}_2\text{O}$ , at  $25^\circ$ , is summarized in Fig. 685. He did not obtain the tetranitrate, but observed, as solid phases, the hexahydrate and the enneahydrate.

According to J. M. Ordway, the *enneahydrate*,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , is deposited from soln. containing  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O} + n(2\text{HNO}_3 \cdot 3\text{H}_2\text{O})$ . The range of stability is

indicated in F. K. Cameron and W. O. Robinson's diagram, Fig. 684, *i.e.* in soln. containing 30 to 45 per cent.  $\text{N}_2\text{O}_5$ , at  $25^\circ$ . G. Malquori obtained the enneahydrate from soln. with between 5.99 per cent.  $\text{Fe}_2\text{O}_3$ , 45.84 per cent.  $\text{N}_2\text{O}_5$ , and 9.25 per cent.  $\text{Fe}_2\text{O}_3$ , 46.48 per cent.  $\text{N}_2\text{O}_5$ . S. Hausmann, and C. F. Schönbein obtained the *hexahydrate*,  $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , by evaporating the aq. soln. to a syrup, and adding half its vol. of nitric acid; R. Wildenstein, by allowing a conc. soln. of iron in nitric acid to stand for 18 months; A. Scheurer-Kestner, by crystallization from the mother-liquor after the separation of the enneahydrate; J. M. Ordway, by heating the enneahydrate until 14 per cent. of water has been expelled, and then adding nitric acid, or by cooling a soln. of a mol. of the fused enneahydrate with 4 mols. of nitric acid; and G. Malquori, by the action of conc. nitric acid on a sat. soln. of the enneahydrate in nitric acid of sp. gr. 1.52. According to J. M. Ordway, the salt is best obtained from a soln. with  $\text{Fe}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + n\text{HNO}_3 \cdot \text{H}_2\text{O}$ —if more water is present, the enneahydrate appears, and if less, the soln. crystallizes with difficulty. G. Malquori said that at  $25^\circ$ , the salt is stable with soln. containing 9.25 to 9.28 per cent.  $\text{Fe}_2\text{O}_3$  and 46.48 to 48.88 per cent.  $\text{N}_2\text{O}_5$ —*vide supra*, Fig. 684. A. Ditte reported a *trihydrate*,  $\text{Fe}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ , to be formed by evaporating a soln. containing a large excess of nitric acid; saturating the syrupy liquid with  $\text{HNO}_3 \cdot \text{H}_2\text{O}$  at  $60^\circ$ ; and draining the crystals on a porous tile. A. Scheurer-Kestner could not confirm the existence of this salt; he said that the *monohydrate*,  $\text{Fe}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ , separates from a soln. supersaturated on the water-bath and then cooled to  $0^\circ$ . J. M. Ordway could not prepare the monohydrate. The hydrates were studied by E. N. Gapon.

**The physical properties of ferric nitrate.**—The enneahydrate was said by C. F. Schönbein, and E. Schaer to furnish pale lavender-blue, amethyst-blue, or purple-coloured rhombic prisms. If pure, the salt is colourless. When heated the colourless salt appears yellow or orange, but on cooling, it becomes colourless again. J. M. Ordway said that the crystals are probably monoclinic, and H. Frey, rhombohedral. N. I. Surgunoff, and B. Lambert and J. C. Thomson obtained colourless or white crystals, which, according to N. I. Surgunoff, are monoclinic with the axial ratio  $a : b : c = 1.1296 : 1 : 1.9180$ , and  $\beta = 131^\circ 31'$ . K. P. Grinakowsky thought that the crystals occur in two modifications. R. Wildenstein, and J. M. Ordway said that the hexahydrate forms water-clear, cubic crystals; and S. Hausmann, and A. Scheurer-Kestner said that the hexahydrate forms colourless prisms. A. Ditte also said that the trihydrate furnishes colourless needles; and A. Scheurer-Kestner, that the monohydrate appears as a colourless, crystalline mass. C. Leenhardt studied the speed of crystallization of the hydrate.

According to J. M. Ordway, the crystals of the enneahydrate have a **specific gravity** of 1.6835 at  $21^\circ$ , and when melted and supercooled to  $21^\circ$ , the sp. gr. is 1.6712. K. P. Grinakowsky found the sp. gr. of the undercooled molten enneahydrate to be, at  $\theta/4^\circ$ :

Sp. gr.	0.2°	9.7	20.7°	50.6°	65.2°
	1.7159	1.7064	1.6979	1.6599	1.6429

B. Franz gave for the sp. gr. of aq. soln. of the salt at  $17.5^\circ/4^\circ$ :

$\text{Fe}(\text{NO}_3)_3$ .	5	10	20	30	40	50	60	65 per cent.
Sp. gr.	1.0398	1.0770	1.1612	1.2622	1.3746	1.4972	1.6572	1.7532

Some observations were made by J. Traube, A. Hauke, F. K. Cameron and W. O. Robinson, A. Heydweiller, C. E. Richards and R. W. Roberts, G. Piaggese, G. T. Gerlach, and H. C. Jones and F. H. Getman. According to B. Cabrera and E. Moles, the sp. gr., at  $19^\circ/4^\circ$ , of soln. with:

$\text{Fe}(\text{NO}_3)_3$	0.0129	0.0534	0.0584	0.1157	0.2204 millimol per litre.
Sp. gr.	1.0029	1.0087	1.0098	1.0209	1.0419

P. F. Gaehr expressed the relation between the sp. gr.,  $D$ , and the percentage concentration,  $C$ , by  $\log_{10} D = aC$ , where  $a$  is a constant. F. K. Cameron and

W. O. Robinson measured the sp. gr. of soln. of ferric oxide in nitric acid of various concentrations; and B. Cabrera and E. Moles, the effect of nitric acid on the sp. gr. of soln. of ferric nitrate. J. Traube discussed the mol. solution vol.

M. Torre measured the **diffusion**,  $D$ , of soln. of ferric nitrate of concentration  $C$  grms.  $\text{Fe}(\text{NO}_3)_3$  per 100 c.c., by the changes in concentration at different temp., in 24 hrs.:

	$C=0.804$			$C=0.320$			$C=0.160$		
	30°	40°	50°	30°	40°	50°	30°	40°	50°
$D$	0.290	0.349	0.407	0.114	0.134	0.161	0.059	0.067	0.081

K. P. Grinakowsky measured the **surface tension**,  $\sigma$  dynes per cm., the **molar surface energy**,  $\sigma v M^{\frac{2}{3}}$ —1.13, 22—and the temp. coeff. of the molar surface energy of undercooled molten enneahydrated ferric nitrate, and found:

	0.5°	9.6°	20.7°	50.6°	65.3°
$\sigma$	70.05	69.42	68.75	66.18	63.35
$\sigma v M^{\frac{2}{3}}$	4240.0	4217.0	4188.0	4105.3	3947.1
$d(\sigma v M^{\frac{2}{3}})/d\theta$	—	2.55	2.65	2.76	10.76

He also found the **viscosity** of the undercooled enneahydrate at 0.3°, 20.6°, and 50.5 to be respectively 6.0336, 1.0653, and 0.2234 grm. per cm. per sec. H. C. Jones and co-workers found the mol. **lowering of the freezing-point**,  $\Delta$ , of soln. with  $C$  mols per litre to be:

$C$	0.0748	0.1496	0.4488	1.0472	1.4960
$\Delta$	6.39	6.37	7.63	10.92	14.30

Enneahydrated ferric nitrate, like  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , shows a greater lowering of the f.p. than is the case with the hexahydrated nitrates of magnesium, zinc, cobalt, and nickel; and it is four or five times as great as the value calculated on the assumption that the solvent and solute are independent. J. S. Anderson observed that the enneahydrate smells of nitric acid; A. Scheurer-Kestner, that some nitric acid is lost at 50°—C. Leenhardt said at 80°; and J. M. Ordway found that about half its nitric acid is lost at 100° and a dry, deliquescent, dark brown powder remains. According to C. Montemartini and E. Vernazza, the dehydration of ferrous nitrate hexahydrate at the ordinary temp. in an atmosphere of carbon dioxide is accompanied by evolution of nitric oxide, and oxidation of the iron:  $3\text{Fe}(\text{NO}_3)_2 + 7\text{H}_2\text{O} \rightarrow 3\text{Fe}(\text{OH})_3 + 5\text{HNO}_3 + \text{NO}$ . Decomposition in boiling aq. soln. in an atmosphere of carbon dioxide, is at first slow with formation of a reddish precipitate; it then suddenly becomes violent and continues to completion according to the above scheme. The preliminary period is shorter for more concentrated solutions or on addition of nitric or nitrous acid, but no definite relation between concentration and the formation of nitrogen dioxide, nitrous oxide, ammonia, etc., was found. The solid product is the hydrate,  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ . S. U. Pickering found that in sunlight, acid vapours are given off at ordinary temp., but they are re-absorbed in darkness. By repeatedly heating the salt above its m.p., K. P. Grinakowsky noticed that the salt is decomposed; F. K. Bell and W. A. Patrick, that with 6 to 8 hrs' heating at 120°, a dry, red basic nitrate is formed; and J. M. Ordway, that at a red-heat all the nitrate is lost, and ferric oxide remains. J. M. Ordway said that the **melting-point** of the enneahydrate is 47.2°; and K. P. Grinakowsky, 50.1°. J. M. Ordway noted that the molten salt remains as a clear, dark red liquid down to 21°. S. Hausmann said that the hexahydrate melts at 35°; C. F. Schönbein gave 50°; and J. M. Ordway, between 35° and 40°. K. P. Grinakowsky, and C. Leenhardt studied the **rate of crystallization** of the undercooled enneahydrate. J. M. Ordway gave 125° for the **boiling-point** of the enneahydrate.

M. Berthelot gave for the **heat of formation**  $(\text{Fe}, \frac{3}{2}\text{N}_2, \frac{3}{2}\text{O}_2, \text{Aq.}) = 157.15$  Cals.; and for  $\text{Fe}_2\text{O}_3 \cdot \frac{9}{2}\text{H}_2\text{O} + 6\text{HNO}_{3\text{soln.}} = 2\text{Fe}(\text{NO}_3)_3 + 35.4$  Cals., and J. Thomsen, 33.95 Cals. J. Thomsen found for the reaction in soln.,  $3\text{Ba}(\text{NO}_3)_2 + \text{Fe}_2(\text{SO}_4)_3 = 2\text{Fe}(\text{NO}_3)_3 + 3\text{BaSO}_4 + 25.776$  Cals. M. Berthelot gave -9.0 Cals. per mol. for



the **heat of solution** of the enneahydrate; and he said that the **heat of dilution** changes with age, because 12 litres of a fresh soln. of a mol of the salt in 6 litres absorbed 1.1 Cals. when diluted with 30 litres of water, but in 3-weeks-old soln., absorbed only 1.05 Cals.—this does not amount to much, after all. The negative heat of soln. is characteristic of **freezing mixtures**, and A. Scheurer-Kestner found that by the dissolution of 2 parts of the enneahydrate in 1 part of water, the temp. is lowered 18.5°.

A. Hauke measured the **index of refraction**, and found for a soln. with 16.65 per cent.  $\text{Fe}(\text{NO}_3)_3$ ,  $\mu=1.3649$  for Na-light, 1.3673 for Tl-light, and 1.3625 for C-light; and for the relation between the **wave-length**,  $\lambda$ , of light, and the refractive index of a soln. with 0.996 grm. of water per c.c. of soln., at 17°, C. E. Richards and R. W. Roberts gave:

$\lambda$ . . .	5893	5780	5461	5330	5218	5105
$\mu$ . . .	1.3797	1.3804	1.3818	1.3827	1.3836	1.3868

and for soln. with varying **concentration**, having  $C$  mol of the salt per litre, at 0°, H. C. Jones and F. H. Getman observed with Na-light:

$C$ . . .	0.0748	0.1496	0.04488	0.7480	1.0470	1.4960
$\mu$ . . .	1.32689	1.33191	1.34536	1.35797	1.37075	1.38873

G. Limann found for the refractive index of soln. with  $C$  equivalents of the salt per litre, at 18°:

$C$ . . .	0	0.5	1	2	4
$\mu$ { $H\alpha$ -line . . .	1.33139	1.33858	1.34562	1.35946	1.38635
$D$ -line . . .	1.33322	1.34054	1.34769	1.36178	1.38917
$H\beta$ -line . . .	1.33737	1.34504	1.35248	1.36713	1.39571
$R$ . . .	35.93	35.90	35.89	35.78	35.6

Observations were also made by A. Heydweiller. The **molecular refraction**,  $R$ , obtained by A. Hauke, for a 16.65 per cent. soln. for the  $C$ -line, is 73.0; and G. Limann gave 35.84 at 18° for Na-light; and the results by A. Heydweiller are indicated above. A. Heydweiller, and G. Limann calculated values for the dispersion. A. Heydweiller discussed the relation between the optical properties and the electrical conductivity of the soln.

The colour of aq. soln. of ferric nitrate is conditioned by hydrolysis—*vide infra*. According to A. Byk and H. Jaffe, the **absorption spectrum** shows a band in the ultra-violet, and it is displaced in the direction of the short wave-lengths by dilution, or by the addition of nitric acid. J. S. Anderson found for the extinction coeff.,  $k$ , of soln. with  $C$  mols of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  per litre:

$\lambda$ . . .	4340	4990	5470	6020	6870	7460	8370	9680	11,750
$k$ { $C=2.0$ . . .	7.3	2.25	0.70	0.16	0.17	0.25	0.32	0.13	0.01
$C=0.2$ . . .	10.6	4.04	0.82	—	—	0.37	0.95	0.21	0.04

for the effect of varying the concentration of the soln.:

	$\lambda=4530$					$\lambda=6530$		
$C$ . . .	2.0	1.4	0.8	0.2	0.02	2.0	1.4	0.8
$k$ . . .	5.57	5.95	6.48	10.49	13.15	0.14	0.15	0.16

Observations were also made by R. A. Houstoun, R. A. Houstoun and C. Cochrane, T. Ewan, C. E. Richards and R. W. Roberts, and R. A. Morton and R. W. Riding.

M. E. Verdet found that the **magnetic rotatory power**—*i.e.* the magnetic rotation of the plane of polarization of light—is smaller for soln. of ferric nitrate than it is for water; the effect becomes almost zero for very conc. soln., but it does not attain a negative value. C. E. Richards and R. W. Roberts observed that the sp. rotation,  $\omega$ , and the value calculated for  $\text{Fe}(\text{NO}_3)_3$ , of a soln. with 0.996 grm. of water per c.c. of soln., at 20°, in a magnetic field of 13,510 gauss, and light of wave-length,  $\lambda$ :

$\lambda$ . . .	5893	5780	5461	5330	5218	5105
$\omega$ . . .	0.0085	0.0090	0.0096	0.0096	0.0099	0.0104
$\omega\text{-Fe}(\text{NO}_3)_3$ . . .	-0.0050	-0.0050	0.0061	0.0069	0.0073	0.0077

There is an absorption band for  $\lambda=5350$ . The value of  $\omega$  increases with a rise of temp. P. K. Pillai, E. Miescher, and F. Allison and E. J. Murphy studied the magneto-optic properties.

M. Schneider could detect no reduction of aq. soln. of ferric nitrate in **sunlight**, but W. H. Ross, and O. Baudisch and E. Mayer observed that in **ultra-violet light**, reduction to ferrous nitrate occurs with the evolution of oxygen. S. U. Pickering observed that the enneahydrate in sunlight gives off acid fumes which are re-absorbed in darkness.

The **electrical conductivity** of aq. soln. of ferric nitrate was measured by H. C. Jones and co-workers, and by A. Heydweiller. H. C. Jones and C. A. Jacobson gave for the mol. conductivity of soln.,  $\mu$ , with a mol of the nitrate in  $v$  litres :

$v$	2	8	16	32	128	512	1024	2048
$\left\{ \begin{array}{l} 0^\circ \\ 10^\circ \\ 25^\circ \\ 35^\circ \end{array} \right.$	$\left\{ \begin{array}{l} 97.68 \\ 128.1 \\ 181.6 \\ 220.7 \end{array} \right.$	$\left\{ \begin{array}{l} 132.2 \\ 185.7 \\ 266.5 \\ 328.2 \end{array} \right.$	$\left\{ \begin{array}{l} 150.7 \\ 202.7 \\ 295.3 \\ 364.3 \end{array} \right.$	$\left\{ \begin{array}{l} 171.4 \\ 233.7 \\ 342.6 \\ 422.6 \end{array} \right.$	$\left\{ \begin{array}{l} 199.5 \\ 271.7 \\ 399.4 \\ 491.4 \end{array} \right.$	$\left\{ \begin{array}{l} 371.3 \\ 408.7 \\ 705.7 \\ 927.0 \end{array} \right.$	$\left\{ \begin{array}{l} 490.9 \\ 571.4 \\ 877.7 \\ 1116.5 \end{array} \right.$	$\left\{ \begin{array}{l} 585.2 \\ 693.5 \\ 961.6 \\ 1183.0 \end{array} \right.$

A. A. Noyes and B. F. Brann showed that the conductivity of a freshly-prepared soln. of  $0.1N\text{-Fe(NO}_3)_3$  changes in some weeks at ordinary temp., or in a couple of hours at  $50^\circ$  to  $55^\circ$ . A. Heydweiller gave 123 for the limiting value of the eq. conductivity at  $18^\circ$ ; and H. C. Jones and F. H. Getman, 190.6 for the limiting value of the mol. conductivity at  $0^\circ$ . A. Heydweiller discussed the relation between the optical properties and the eq. conductivity of aq. soln. of ferric nitrate. H. C. Jones and F. H. Getman calculated for the percentage **degree of ionization**,  $\alpha$ , and obtained for the mol. conductivity of soln. with a mol. of the salt in  $v$  litres at  $0^\circ$  :

$v$	0.67	0.74	0.95	1.34	2.23	2.34	6.68	13.37
$\mu$	43.2	48.2	63.4	82.0	102.0	117.2	136.4	152.5
$\alpha$	22.6	25.3	33.3	43.0	53.5	61.5	71.6	80.0

H. C. Jones and C. A. Jacobson observed that the value of  $\alpha$  increases with a rise of temp., owing to hydrolysis. H. C. Jones and F. H. Getman calculated values for the **solvation** or **degree of hydration** of ferric nitrate in aq. soln. For soln. with  $C$  mols of  $\text{Fe(NO}_3)_3$  per litre,  $[\text{H}_2\text{O}]$ , represented the number of mols in combination with a mol of salt if a litre of the soln. at the given concentration, contained 1000 grms. of water :

$C$	1.4960	1.3464	1.0472	0.7480	0.4488	0.2992
$[\text{H}_2\text{O}]$	28	29	33	37	43	37

As indicated above, the salt is hydrolyzed in aq. soln. The degree of hydrolysis is dependent on the conc., the age, the temp., the acidity, and the presence of other substances in the soln. The progress of the hydrolysis is shown by the changes of colour which occur, for this is determined by the presence of colloidal hydrated ferric oxide:  $\text{Fe(NO}_3)_3 + 3\text{H}_2\text{O} \rightleftharpoons \text{Fe(OH)}_3 + 3\text{HNO}_3$ , so that the colour changes through yellow, brown, and red, after which, a turbidity appears. Thus, S. U. Pickering observed that the colour of the aq. soln. increases in intensity with progressive dilution until a maximum is attained, after which the colour becomes paler with dilution. G. Wiedemann gave for the percentage degree of hydrolysis,  $H$ , of soln. with  $C$  grms. of  $\text{Fe(NO}_3)_3$  per 100 c.c. at  $20^\circ$  :

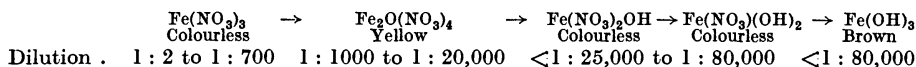
$C$	50.03	37.51	24.99	18.75	12.47	6.24
$H$	12.0	13.9	14.4	14.0	14.9	17.7

U. Antony and G. Gigli found for soln. 10 days old :

$C$	50 to 6.7	4.0	2.0	0.5	0.2	0.05	0.02	0.005	0.004
$H$	7	13	16	26	30	44	55	14.9	17.7

The formation of colloidal hydrated ferric oxide is shown by the fact that sodium chloride precipitates ferric hydroxide, and that potassium ferrocyanide gives no

blue coloration in such solutions ; in less dilute solution, to which ferrocyanide has been added, the blue colour gradually increases in intensity owing to the continued re-formation of the ferric nitrate. Aq. solutions of ferric nitrate containing less than 0.1 per cent. are quite colourless, thus differing from other dil. soln. of ferric salts which are always coloured ; it is supposed that in such dil. ferric nitrate soln., basic ferric salts are not formed, but rather salts of pyronitric acid,  $\text{H}_4\text{N}_2\text{O}_7$ , or orthonitric acid,  $\text{H}_5\text{NO}_5$ . Ferric orthonitrate and pyronitrate being simply products of hydrolysis of ferric nitrate, the reaction between all three salts and water is a reversible one ; the orthonitrate by further hydrolysis dissociates into ferric hydroxide and nitric acid. U. Antony and G. Gigli thus concluded that the successive stages of the hydrolysis are :



R. Weinland attributed the amethyst tint, observed by S. U. Pickering with conc. soln., to the formation of a pale red hexaquoferic cation. J. S. Anderson showed that a soln. with over 0.8 mol of the nitrate per litre remained clear under conditions where a soln. with 0.2 mol per litre became turbid in a year, and with a soln. having 0.02 mol per litre, the precipitation of the hydrated ferric oxide was complete, and the soln. decolorized. The progress of the hydrolysis by colour-changes was also observed by U. Antony and G. Gigli, and, as indicated above, by A. A. Noyes and B. F. Brann. C. F. Schönbein observed that by raising the temp. of an aq. soln. of ferric nitrate, the colour deepens as it passes from yellow to brown to red, and that when the soln. is cooled the liquid becomes paler in tint. Analogous observations showing that the progress of the hydrolysis is favoured by raising the temp. were made by F. Beilstein and R. Luther, M. Berthelot, T. Cohen, E. J. Houstoun, S. U. Pickering, E. Schaer, E. A. Schneider, and A. A. Noyes and B. F. Brann. G. Wiedemann observed almost a linear relation between the percentage degree of hydrolysis,  $H$ , and the temp. between  $10^\circ$  and  $60^\circ$  for a soln. of the nitrate with 1.155 grms. Fe in 10 c.c. :

	6°	15°	20.5°	25°	31.5°	41°	51°	55.3°	62°
$H$	9.6	10.3	12.5	13.5	15.5	16.6	18.7	19.3	21.4

According to J. M. Ordway, and A. Scheurer-Kestner, the brown aq. soln. of ferric nitrate becomes colourless if a little nitric acid be added. A similar observation was made by A. A. Noyes and B. F. Brann. F. K. Cameron and W. O. Robinson said that the brown colour disappears when a mol of  $\text{HNO}_3$  is present per mol of  $\text{Fe(NO}_3)_3$ , and S. U. Pickering said that when 1.2 to 1.8 mols of  $\text{HNO}_3$  are present per gram-atom of iron, the dil. soln. is yellow ; with 3 to 20 mols of nitric acid, the colour is lemon-yellow. G. Wiedemann examined the effect of nitric acid on the degree of hydrolysis of ferric nitrate soln. C. F. Schönbein, and E. Schaer observed the effect of various additions on the colour-changes of the soln. ; G. Wiedemann, the degree of hydrolysis of basic nitrate in aq. soln. ; and S. Miyamoto, the decomposing action of the silent discharge.

A. A. Groening and H. P. Cady measured the **decomposition voltage** of soln. of ferric nitrate in water and in liquid ammonia, and obtained 1.02 and 1.19 volts respectively ; and the metal over-voltages are respectively 0.15 and -0.8 volt. A. Schukareff observed a **magnetochemical effect** in the electrolysis of a soln. of ferric nitrate with platinum electrodes when the cathode is in a magnetic field, but not so with the anode in a magnetic field.

M. Faraday found enneahydrated ferric nitrate to be paramagnetic ; and A. Quartaroli showed that if the aq. soln. is not too dilute, it also is paramagnetic, but very dilute soln. are diamagnetic. The concentration of the soln. where the diamagnetism of water just neutralizes the paramagnetism of the ferric nitrate is 2.94 grms. Fe per litre. Observations on the **magnetic properties** of the soln. were made by J. Plücker, and G. Wiedemann. J. S. E. Townsend gave  $62 \times 10^{-6}$

mass unit for the **magnetic susceptibility** of the aq. soln. at  $10^\circ$ ; O. Liebknecht and A. P. Wills,  $56 \times 10^{-6}$  at  $18^\circ$ ; and G. Jäger and S. Meyer,  $46 \times 10^{-6}$  at  $18^\circ$ . G. Jäger and S. Meyer measured the effect of variations in the field-strength between 10,000 and 18,000 gauss, and J. S. E. Townsend, between 1 and 9 gauss, and observed no perceptible influence on the susceptibility. L. A. Welo's results for the solid and fused salt are indicated in Fig. 580. B. Cabrera and E. Moles gave for the sp. and the at. susceptibility of aq. soln. of ferric nitrate, between  $16.6^\circ$  and  $18.3^\circ$ :

$\text{Fe}(\text{NO}_3)_3$	.	.	0.5304	1.292	1.412	2.837	5.530 per cent.
Specific $\chi \times 10^6$	.	.	-0.4378	-0.03579	0.03014	0.8359	2.2933
Atomic $\chi \times 10^6$	.	.	12.755	12.665	12,730	13,145	13,550

The results for soln. with 1.285 grms.  $\text{Fe}(\text{NO}_3)_3$  per 100 grms. of soln. containing free nitric acid in the proportion  $q$  mol  $\text{HNO}_3$  : mol.  $\text{Fe}(\text{NO}_3)_3$ :

$q$	.	.	0.1876	0.3377	0.8646	1.3371	2.714
$\chi \times 10^6$	.	.	0.0860	0.2227	0.6172	0.6750	0.7465

Observations were also made by G. Piaggese, and A. Quartaroli; the last-named gave for the mol. susceptibility of soln. with a mol of salt in  $v$  litres, at  $18^\circ$ :

$v$	.	.	10	100	250	500	1,000
$\chi \times 10^6$	.	.	12,789	12,272	11,859	11,860	11,545

J. S. E. Townsend found that at  $10^\circ$ , in a field of 1 to 9 gauss, there is a linear relation between the susceptibility, and the degree of dilution. G. Wiedemann, G. Piaggese, and A. E. Oxley observed a linear relation between the susceptibility and temp. G. Piaggese found for soln. of the percentage concentration  $C$ , with a field of intensity  $H$  gauss:

$\chi \times 10^6$	$H=4100; C=42.819$				$H=7460; C=7.325$			
	$24.2^\circ$	$40.3^\circ$	$71.5^\circ$	$84.7^\circ$	$23.7^\circ$	$41.2^\circ$	$63.5^\circ$	$85.4^\circ$
	27.521	26.289	24.667	23.185	3.247	3.077	2.898	2.703

H. Mosler observed that the temp. coeff. with soln. containing 12.1, 16.4, 21.2, and 28.2 per cent.  $\text{Fe}(\text{NO}_3)_3$ , are respectively -0.00273, -0.00287, -0.00286, and -0.00287, between  $0^\circ$  and  $40^\circ$ ; whilst G. Piaggese gave for soln. with 7.32, 19.51, and 42.82 per cent.  $\text{Fe}(\text{NO}_3)_3$ , the respective values -0.00287, -0.00285, and -0.00276 between  $23^\circ$  and  $85^\circ$ . Observations were also made by G. Jäger and S. Meyer. According to L. A. Welo, the magnetic susceptibilities of solid and liquid enneahydrate are summarized in Fig. 580. The Curie constants,  $C=\chi(T-\theta)$ , for the solid are,  $C=4.25$ , and  $\theta=0^\circ$ ; and for the liquid,  $C=1.78$ , and  $\theta=164^\circ$ . B. Cabrera and E. Moles, and A. Quartaroli made estimates of the **magneton number** for ferric nitrate in aq. soln.

**The chemical properties of ferric nitrate.**—S. Miyamoto said that in the silent electric discharge, in hydrogen, the hydroxide, nitric oxide, nitrogen dioxide, and ammonium nitrate and nitrite are formed. W. Ipatéeff and A. I. Kisseleff, and W. Ipatéeff found that **hydrogen** at about 200 atm. press. acts on a soln. of iron nitrate precipitating hydrated ferric oxide, or a mixture of ferrous and ferric oxides; metallic iron was not formed even at  $360^\circ$ . C. F. Schönbein noticed the reduction of a soln. of ferric nitrate by nascent hydrogen; and F. F. Runge, its reduction by zinc amalgam. H. Frey found the enneahydrate to be very deliquescent in **air**; and A. Scheurer-Kestner, and N. I. Surgunoff added that a brown liquid is produced which readily decomposes when heated, for it gives off nitric acid fumes at  $50^\circ$ . C. F. Schönbein observed that the hexahydrate deliquesces to a honey-yellow liquid. J. M. Ordway, A. Scheurer-Kestner, and F. K. Cameron and W. O. Robinson found that the enneahydrate dissolves in **water** in all proportions, forming a brown or yellowish-brown soln.; but G. Malquori added that the solubility at  $25^\circ$  is 46.57 per cent.—*vide* Figs. 686 and 689,  $\text{Fe}(\text{NO}_3)_3$ . J. M. Ordway observed that the hexahydrate readily takes up 3 mols. of water to form the

enneahydrate; C. F. Schönbein added that the hexahydrate dissolves in water in all proportions. The relations of the nitrate with water have been discussed in connection with the solubility of the salt; and also in connection with the hydrolysis of aq. soln. V. L. Bohnson, and I. S. Teletoff and V. M. Simonova studied the catalytic action of ferric nitrate on **hydrogen dioxide**—*vide supra*, ferric chloride.

Many **basic salts** have been reported, but F. K. Cameron and W. O. Robinson could find none; and they consider to be solid soln. all the basic nitrates which have been reported; remembering their results with the basic ferric sulphates, it is possible that some of the basic nitrates which have been reported, or are yet to be reported as being formed under other conditions, may be chemical individuals. U. Antony and G. Gigli assumed that definite individuals are formed as intermediate products in the hydrolysis of aq. soln. of the nitrate—*vide supra*, the hydrolysis of this salt, and also in connection with the basic carbonates. A. Müller, and E. Lenssen regarded commercial *iron-liquor* as a soln. of basic nitrates. J. M. Ordway said that a mol. of  $N_2O_5$  forms compounds with 1, 2, 3, 4, 5, 6, and 8 mols. of ferric oxide, and that they are soluble in water. These substances can be prepared as colloidal soln. by dissolving the calculated quantity of freshly-precipitated, hydrated ferric oxide in an aq. soln. of ferric nitrate. Soln. containing 6 mols. of ferric oxide to 1 mol. of  $N_2O_5$  furnish precipitates, when treated with various salts—*e.g.*, sodium or ammonium chloride; potassium iodide or chlorate; sodium, calcium, zinc, or copper sulphate; potassium, sodium, ammonium, magnesium, barium, or lead nitrate; and barium or zinc acetate; but not by alcohol, lead or copper acetate, mercuric cyanide, silver nitrate, or arsenious acid. The phenomenon resembles the flocculation of colloids by electrolytes—*vide supra*, ferric chloride, and the hydrosol and hydrogel of hydrated ferric oxide.

Taking the mol. ratios in this order:  $Fe_2O_3 : N_2O_5 : H_2O$ , S. Hausmann reported what he regarded as 36:1:48; A. Béchamp, 12:1:0; A. Béchamp, S. Hausmann, and J. M. Ordway, 8:1:12; J. M. Ordway, 6:1:*n*; and also 5:1:*n*; J. J. Berzelius, P. Grouvelle, S. Hausmann, J. M. Ordway, C. F. Schönbein, and A. Scheurer-Kestner, 4:1:*n*; A. Scheurer-Kestner, and J. M. Ordway, 3:1:2; J. M. Ordway, 3:3:*n*; A. Benrath, J. M. Ordway, A. Piccini and F. M. Zucco, and A. Scheurer-Kestner, 2:1:1; J. M. Ordway, and A. Scheurer-Kestner, 1:1:*n*; J. M. Ordway, 2:3:*n*; G. Lemoine, J. M. Ordway, and A. Scheurer-Kestner, 1:2:*n*; and J. M. Ordway, 2:5:*n*.

C. F. Schönbein, and E. Schaer discussed the colour-changes which occur when **potassium bromide**, or **sulphur dioxide** is added to the aq. soln. C. F. Schönbein noted the reducing action of sulphur dioxide as well as of **selenium and tellurium hydrides**. A. W. Davidson found that the enneahydrate with 100 per cent. **sulphuric acid** forms yellowish-white, insoluble ferric sulphate. C. F. Schönbein, and E. Schaer discussed the colour-changes which occur when **ammonium chloride** is added to the aq. soln. H. Davy observed that a soln. of ferric nitrate absorbs little or no **nitric oxide**; and C. F. Schönbein observed that this gas reduces a soln. of ferric nitrate. W. Heldt, and E. S. Hedges found that with an increasing concentration of **nitric acid**, the solubility of the nitrate is reduced; J. M. Ordway found that 100 parts of nitric acid of sp. gr. 1.37 do not quite dissolve 5 parts of the enneahydrate at 15.6°. C. F. Schönbein observed that **phosphorus** slowly reduces a soln. of ferric nitrate; and similarly with **phosphine**; **arsenic, antimony, and bismuth** also reduce the soln., as does **stibine**. C. F. Schönbein, and E. Schaer discussed the colour-changes which occur on the addition of **arsenic trioxide** to a soln. of ferric nitrate.

When the soln. is shaken up with **carbon** powder, it is reduced forming ferrous nitrate and a basic ferric nitrate. C. F. Schönbein, and E. Schaer discussed the colour-changes which occur when **methyl** or **ethyl alcohol** is added to the aq. soln. A. Scheurer-Kestner observed that the enneahydrate forms a brown soln. with alcohol, but, added J. M. Ordway, the solution is incomplete. E. Schaer observed

that the soln. in 97 to 98 per cent. alcohol is not stable, and decomposes in a few weeks at ordinary temp. or when warmed, depositing a basic nitrate. A. Benrath observed that in the photochemical oxidation of alcohol by ferric nitrate, the ferric salt is not reduced to the ferrous state, but a basic ferric nitrate is precipitated. A. Naumann observed that the enneahydrate dissolves in **acetone** of sp. gr. 0.795. R. Weinland and co-workers, A. Rosenheim and P. Müller, and E. Späth discussed the action of **acetic acid** on the ennea- and hexahydrates; a complex salt appears to be formed. The complex salts were studied by R. Grünberg-Krasnowskaja, and R. Weinland and H. Hachenburg. C. F. Schönbein observed that the acid reduces a hot soln. of ferric nitrate, and that the reduction is incomplete in the cold; similar results were obtained with **formic, citric, tartaric, and uric acids**; C. F. Schönbein, and E. Schaer observed the effect of tartaric and citric acids on the hydrolysis of ferric nitrate. C. F. Schönbein observed that not only is **oxalic acid** not oxidized by soln. of ferric nitrate, but that the acid hinders the reduction of the nitrate by other organic and inorganic substances, but G. Lemoine said that the oxalic acid is oxidized with the evolution of carbon dioxide and nitrogen peroxide, and the formation of a precipitate of basic ferric nitrate and ferric oxide. U. Antony and G. Gigli discussed the action of **potassium ferrocyanide** on ferric nitrate. R. Weinland and A. Kissling studied the compounds formed with **quinoline**. G. Spacu obtained a complex with **benzidine**, and G. A. Barbieri, one with **urea**. C. F. Schönbein noted the reducing action of **creosote**, and **sugar**; and C. F. Schönbein, and E. Schaer, the decolorization of **indigo**; and the effect of **gum arabic** on the colour of the soln. J. Jettmar discussed the action of ferric nitrate soln. on **animal skins** in the tanning industry. I. Plotnikoff and K. Weber studied the action of the nitrate on **nicotine**; and W. Thomson and F. Lewis, on **india-rubber**.

C. F. Schönbein found that a soln. of ferric nitrate is slowly reduced by some **metals**—copper, silver, zinc cadmium, mercury, tin, lead, and iron; but the action with gold, palladium and platinum is uncertain. M. V. Dover, and A. A. Noyes and B. F. Brann represented the reaction with silver by:  $\text{Ag} + \text{Fe}(\text{NO}_3)_3 \rightleftharpoons \text{AgNO}_3 + \text{Fe}(\text{NO}_3)_2$ , which was also discussed by E. J. Shaw and M. E. Hyde. C. C. Palit and N. R. Dhar noticed that the presence of ferric nitrate retards the dissolution of mercury in nitric acid, but accelerates the action of the acid on copper, and silver. C. F. Schönbein found that the soln. of ferric nitrate is slowly reduced by **cuprous oxide**; and D. Vitali found that **silver oxide** results in the deposition of hydrated ferric oxide; A. Mailhe, that yellow, freshly-precipitated **mercuric oxide** is dissolved, and a basic mercuric nitrate,  $\text{Hg}_2\text{O}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ , is precipitated; E. A. Schneider, that **aluminium hydroxide** is taken up in colloidal soln.; and J. M. Ordway, that **ferric hydroxide** is also taken up in colloidal soln. E. Kothny found that **cupric sulphide**, and **chalcopyrite** are not attacked by a soln. of ferric nitrate, but E. F. Anthon observed that with **lead sulphide** some iron sulphide is formed. According to E. M. Walton, and J. M. Ordway, when the enneahydrate is mixed with hydrated **sodium carbonate** or **hydrocarbonate**, there is a marked drop in temp.; and E. M. Walton, that when the enneahydrate is mixed with hydrated **calcium** or **sodium chloride**, the mixture liquefies, and there is an interchange of acid radicles.

G. Malquori's observations on the ternary system:  $\text{KNO}_3\text{--Fe}(\text{NO}_3)_3\text{--H}_2\text{O}$ , show that no **potassium ferric nitrate** is formed at 25°, but in the presence of nitric acid, potassium ferric nitrate,  $2\text{KNO}_3 \cdot \text{Fe}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$ , is formed as indicated below. The results are summarized in Figs. 686 and 687. G. Malquori studied the quaternary system:  $\text{Fe}(\text{NO}_3)_3\text{--KNO}_3\text{--HNO}_3\text{--H}_2\text{O}$  at 25°, and observed the solid phases  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  with soln. having  $\text{Fe}(\text{NO}_3)_3$ , 28.02 per cent.:  $\text{HNO}_3$ , 54.23; and  $\text{H}_2\text{O}$ , 17.75: the two hydrates and  $2\text{KNO}_3 \cdot \text{Fe}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$  with soln. having  $\text{Fe}(\text{NO}_3)_3$ , 27.00;  $\text{KNO}_3$ , 17.30;  $\text{HNO}_3$ , 39.11;  $\text{H}_2\text{O}$ , 16.59: the enneahydrate and  $\text{KNO}_3$  with  $\text{Fe}(\text{NO}_3)_3$ , 39.05;  $\text{KNO}_3$ , 11.02; and  $\text{H}_2\text{O}$ , 49.03: the enneahydrate, potassium nitrate, and  $\text{Fe}(\text{NO}_3)_3 \cdot 2\text{KNO}_3 \cdot 4\text{H}_2\text{O}$  with  $\text{Fe}(\text{NO}_3)_3$ ,

24.91;  $\text{KNO}_3$ , 26.50;  $\text{HNO}_3$ , 26.71; and  $\text{H}_2\text{O}$ , 21.88; and  $\text{Fe}(\text{NO}_3)_3 \cdot 2\text{KNO}_3 \cdot 4\text{H}_2\text{O}$  and  $\text{KNO}_3$  with  $\text{Fe}(\text{NO}_3)_3$ , 7.80;  $\text{KNO}_3$ , 43.95;  $\text{HNO}_3$ , 46.15; and  $\text{H}_2\text{O}$ , 2.10. The lines  $mMm$ ,  $nNn$ , and  $pP$  represent the systems  $\text{Fe}(\text{NO}_3)_3$ - $\text{HNO}_3$ - $\text{H}_2\text{O}$ ,  $\text{Fe}(\text{NO}_3)_3$ - $\text{KNO}_3$ - $\text{H}_2\text{O}$ , and  $\text{KNO}_3$ - $\text{HNO}_3$ - $\text{H}_2\text{O}$  respectively. Sat. soln. of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O} + \text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  are represented by the line  $MA$ ;  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O} + \text{KNO}_3$ , by  $NB$ ;  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O} + \text{Fe}(\text{NO}_3)_3 \cdot 2\text{KNO}_3 \cdot 4\text{H}_2\text{O}$ , by  $AB$ ;  $\text{Fe}(\text{NO}_3)_3$ .

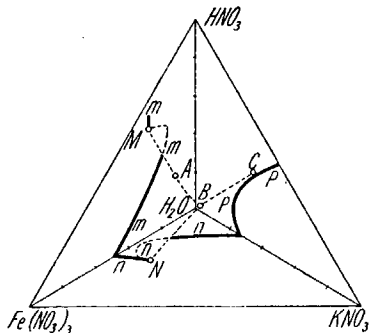


FIG. 686.—The Quaternary System:  $\text{Fe}(\text{NO}_3)_3$ - $\text{KNO}_3$ - $\text{HNO}_3$ - $\text{H}_2\text{O}$ , at  $25^\circ$ .

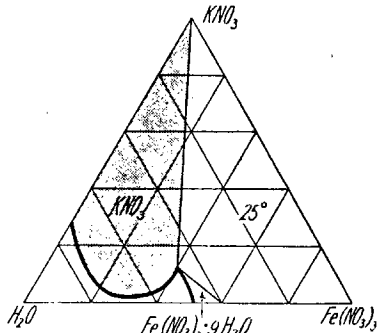


FIG. 687.—Equilibrium in the Ternary System:  $\text{KNO}_3$ - $\text{Fe}(\text{NO}_3)_3$ - $\text{H}_2\text{O}$ , at  $25^\circ$ .

$2\text{KNO}_3 \cdot 4\text{H}_2\text{O} + \text{KNO}_3$ , by  $BC$ . Points  $A$  and  $B$  represent soln. sat. with respect to three salts; and  $C$  represents the solubility of  $\text{Fe}(\text{NO}_3)_3 \cdot 2\text{KNO}_3 \cdot 4\text{H}_2\text{O}$  in a sat. soln. of potassium nitrate in nitric acid of sp. gr. 1.52. H. L. Wells and A. P. Beardsley reported caesium ferric nitrate,  $\text{CsNO}_3 \cdot \text{Fe}(\text{NO}_3)_3 \cdot 7\text{H}_2\text{O}$ , to be formed at a rather low temp. in very conc. soln. of eq. proportions of the component salts in nitric acid. The pale yellow, deliquescent, prismatic crystals melt between  $33^\circ$  and  $36^\circ$ .

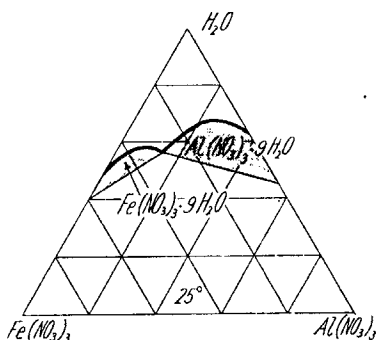


FIG. 688.—Equilibrium in the Ternary System:  $\text{Al}(\text{NO}_3)_3$ - $\text{Fe}(\text{NO}_3)_3$ - $\text{H}_2\text{O}$ , at  $25^\circ$ .

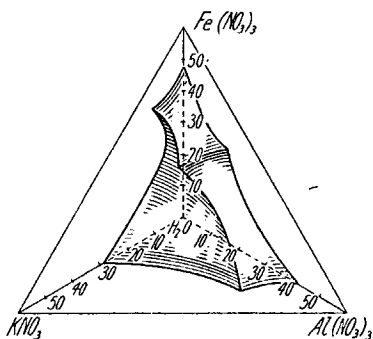


FIG. 689.—Equilibrium Conditions in the Quaternary System:  $\text{KNO}_3$ - $\text{Al}(\text{NO}_3)_3$ - $\text{Fe}(\text{NO}_3)_3$ - $\text{H}_2\text{O}$ , at  $25^\circ$ .

G. Malquori in his study of the ternary system:  $\text{Al}(\text{NO}_3)_3$ - $\text{Fe}(\text{NO}_3)_3$ - $\text{H}_2\text{O}$ , at  $25^\circ$ , observed no formation of an aluminium ferric nitrate; the only solid phases observed were the two enneahydrates as illustrated in Fig. 688. No complex was observed in the quaternary system:  $\text{KNO}_3$ - $\text{Al}(\text{NO}_3)_3$ - $\text{Fe}(\text{NO}_3)_3$ - $\text{H}_2\text{O}$ , at  $25^\circ$ . The results are summarized in Fig. 689.

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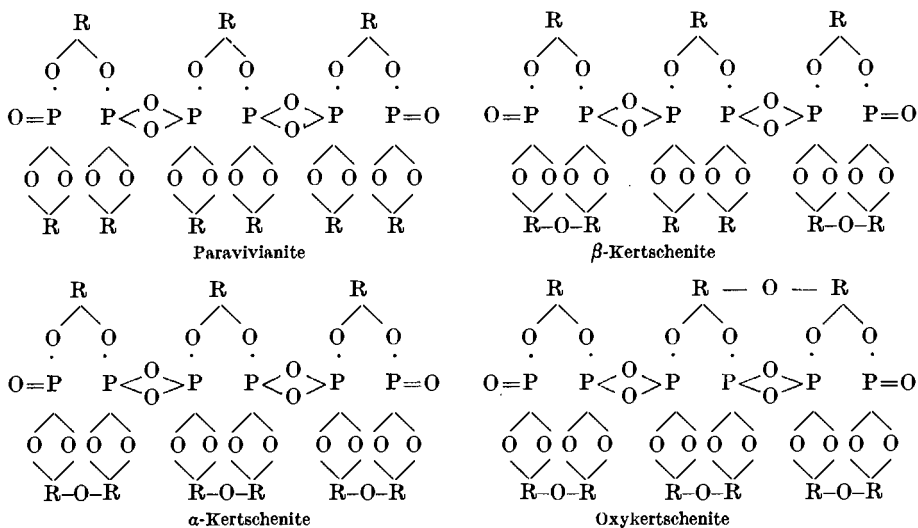


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### § 50. The Ferrous Phosphates

In 1758, A. Cronstedt<sup>1</sup> referred to *calx martis phlogisto juncta*; in 1772, I. Eques a Born referred to *cæruleum berlinense natioum*; in 1783, J. B. L. Romé de l'Île, to *ochre martiale bleue* or *bleue de Prusse natif*; and in 1784, M. H. Klaproth, to *natürliche Berlinerblau*; A. G. Werner applied the term *vivianite*—after J. G. Vivian—to an earth which was afterwards shown to be the same as the *blue iron earth*, or *native prussian blue*. F. Mohs called it *Eisenglimmer*; A. Breithaupt, *Eisenphyllite*; E. F. Glocker, *Glaucosiderit*; T. Thomson, *mullicite*; and P. Berthier, *anglarite*. Analyses, etc., have been reported by M. H. Klaproth, R. Pattison, J. Bostock, J. Murray, L. N. Vauquelin, F. Stromeyer, R. Brandes, A. Vogel,

M. Segeth, P. Berthier, C. F. Rammelsberg, N. S. Maskelyne and W. Flight, W. Fisher, F. Kurlbaum, H. Struve, S. P. Popoff, K. von Muraközy, W. L. Dudley, W. Tjelouchin, J. Thiel, and C. Schmidt. The fresh mineral, not contaminated with impurities, has a composition closely approximating that of **ferrous orthophosphate**,  $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ , but as emphasized by C. F. Rammelsberg, vivianite, as it usually occurs in nature, is rather a mixture of different phosphates:  $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O} + n\text{Fe}_3\text{P}_4\text{O}_{19} \cdot 16\text{H}_2\text{O}$ ; S. P. Popoff also emphasized that the ferrous iron may be isomorphously replaced by calcium, manganese, or magnesium,  $\text{R}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ , where R denotes ferrous iron, Mg, Mn, and Ca, and he called this complex *paravivianite*; and there are a number of specimens containing more or less ferric iron—*e.g.*,  $\text{RO} \cdot \text{Fe}_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot 7\text{H}_2\text{O}$ , or  *$\alpha$ -kertschenite*—after Kertsch, Crimea; and  $5\text{RO} \cdot 2\text{Fe}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5 \cdot 23\text{H}_2\text{O}$ , or  *$\beta$ -kertschenite*. W. L. Dudley represented the composition of the mineral by a doubled formula; and S. P. Popoff the tripled formulæ:



Vivianite, or blue earth, occurs associated with pyrrhotite and pyrite in copper, and other metal veins. It occurs friable and crystallized in beds of clay, and sometimes associated with limonite or bog-iron ore. It also frequently occurs in cavities of fossils or buried bones. Thus, A. Lacroix<sup>2</sup> found it associated with fossil teeth near Bayonne, Basses Pyrénées; P. Gaubert, in mastodon bones, San Pablo, Guatemala; and W. L. Dudley found, near Edgeville, Kentucky, plant roots which were transformed almost completely into blue earth by a process of replacement. J. Schlossberger discussed the formation of blue earth by the action of organic matter, and mentioned that some iron nails found in the stomach of an ostrich were enveloped in black, organic matter, and after several days' exposure to the air became covered with blue spots owing to the formation of the blue phosphate. L. Gmelin added that a pit in a town had been filled for centuries with bones, wood, ferruginous gneiss, etc. Colourless crystals of vivianite were found on the carbonized pieces of wood, and likewise on the micaceous laminae of the gneiss, but not on the other materials; the crystals became blue on exposure to air. W. Haidinger found crystals of vivianite in the hollow of a bone in the skeleton of a miner found in an old working at Tarnowitz. E. V. Shannon found vivianite encrusting a fossil tusk in Idaho; and H. Kunz-Krause discussed its formation in arable soils. Other examples were recorded by F. Sandberger, J. Nicklès, N. Friedreich, N. J. Berlin, and M. Nitschmann. R. Warrington found that a soln. of calcium phosphate in carbonated water is completely decomposed by hydroxides

of iron and aluminium found in clays and soils. The formation of blue earth in peat, and moor soils, etc., was discussed by J. Stansfield, A. F. Wiegmann, F. Senft, K. Rördam, J. M. van Bemmelen, A. Gärtner, and G. Reinders. G. Tammann and H. O. von Samson-Himmelstjerna attributed the blue colour of some artificial preparations to the presence of a ferrous polyphosphate, not ferric phosphate.

C. F. Rammelsberg<sup>3</sup> obtained a white precipitate of ferrous phosphate by adding sodium hydrophosphate to a soln. of a ferrous salt; and the composition of the precipitates was also investigated by G. C. Wittstein, and G. Jenzsch. J. M. van Bemmelen said that if a mixed soln. of 1 of ferrous sulphate, 12 of sodium hydrophosphate, and 1 of glacial acetic acid be kept some days at ordinary temp. out of contact with air, the **colloidal ferrous phosphate** first produced forms a sol with the acetic acid, which gradually deposits crystals of the *octohydrate* of ferrous phosphate,  $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ . E. Angelescu and G. Balanescu found that the simultaneous precipitation of iron and phosphoric acid is possible when the ratio Fe : P is greater than 2, and when the acidity  $p_{\text{H}}$  is less than 7. The temp. and the anion of the ferric salt are without effect on the precipitation. In alkaline soln., the phosphoric acid is not completely adsorbed. W. R. G. Atkins studied the effect of the acidity of the soln. on the composition of ferrous phosphate. H. Debray obtained the normal ferrous phosphate by heating the hydrophosphate with water in a sealed tube at  $250^\circ$ ; E. N. Horsford, by heating mixed soln. of sodium phosphate and ferrous sulphate in an atm. of carbon dioxide in a sealed tube; and E. J. Evans, by allowing a soln. of 2 parts sodium acetate, 10 parts of sodium phosphate, and 8 parts of ferrous sulphate to stand for several days out of contact with air, collecting the precipitate on a calico filter, and drying it at  $40^\circ$ . Small crystals develop if the precipitate be kept in contact with its mother-liquor for a week at  $60^\circ$  to  $80^\circ$ .

G. Cesaro prepared the salt by mixing soln. of ammonium ferrous sulphate and ammonium phosphate, dissolving the precipitate by adding hydrofluoric acid dropwise, and allowing the soln. to stand for a long time. In about 17 days, the small crystals which appear have the composition of vivianite. E. Weinschenk obtained colourless crystals by the action of ammonium hydrophosphate on a soln. of a ferrous salt in a sealed tube at an elevated temp. According to A. C. Becquerel, iron plates immersed in an aq. soln. of ammonium phosphate become covered with white crystalline ferrous phosphate; and if a cell be made up with a porous pot containing a soln. of copper sulphate and a copper rod as cathode, placed in a soln. of sodium phosphate with an iron rod as anode, on closing the circuit, white crystalline nodules of ferrous phosphate collect on the iron rod, and then quickly assume a blue colour on exposure to air.

H. Debray prepared the *monohydrate*,  $\text{Fe}_3(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ , as a dark green, crystalline powder, by heating the hydrophosphate,  $\text{FeHPO}_4$ , with water at  $250^\circ$ . F. Müllbauer obtained the *trihydrate*,  $\text{Fe}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ , as a mineral occurring in the phosphate deposits of Bavaria; and he called it **bauldaufite**—after M. Bauldauf. It is considered to be isomorphous with hydrated manganous phosphate. The light rose, or flesh-red monoclinic prisms have the axial ratios  $a : b : c = 2.21 : 1 : 1.84$ ,  $\beta = 133^\circ 18'$ . The optical character is negative. H. Steinmetz gave the formula:  $\text{R}_5\text{H}_2(\text{PO}_4)_4 \cdot 5\text{H}_2\text{O}$ . P. Dwojtschenko, and S. P. Popoff described a yellow, colloidal phosphate approximating  $3\text{Fe}_2\text{O}_3 \cdot 2\text{P}_2\text{O}_5 \cdot 17\text{H}_2\text{O}$ , from the Crimea; it was called **bosphorite**. A. Gautier said that the *hexahydrate*,  $\text{Fe}_3(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$ , is formed by the prolonged heating at  $83^\circ$  of finely-divided ferrous carbonate in suspension in an aq. soln. of ammonium phosphate; or if a soln. of ferrous carbonate in carbonic acid is heated with ammonium phosphate. The mineral vivianite could have been formed naturally by some such reaction, but at a lower temp., and during a longer period to account for the higher water-content. The *octohydrate*,  $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ , is represented by vivianite.

The mineral is often white when freshly dug up, but it afterwards turns green or blue on exposure to air. This is the case with the colourless crystals from

Delaware, Pennsylvania, observed by W. Fisher. This is taken to indicate that the blue colour is due to the presence of ferric phosphate. The colour deepens on prolonged exposure—*vide infra*. The streak, or powder, is at first colourless to bluish-white, soon changing to indigo-blue. In the extreme case, the powder becomes liver-brown. Vivianite may occur in prismatic crystals sometimes flattened parallel to the (100)-face; and the prismatic faces may be striated. The crystals may occur in stellate groups. Vivianite may form reniform or globular masses, and have a fibrous or earthy structure. The mineral may also occur as an incrustation. G. vom Rath gave for the axial ratios of the monoclinic prisms,  $a : b : c = 0.74975 : 1 : 0.70153$ , and  $\beta = 75^\circ 34\frac{1}{2}'$ ; and G. Cesaro,  $0.7488 : 1 : 0.7020$ , and  $\beta = 104^\circ 33\frac{1}{4}'$ . Observations on the crystals were also made by W. H. Miller, B. Gildersleeve, F. Ulrich, S. Koch, G. Cesaro, A. des Cloizeaux, H. Buttgenbach, E. V. Shannon, and O. Mügge. The (010)-cleavage is nearly perfect; and the (100)-cleavage occurs in traces. The optical character is positive; and the optic axial angles are medium; according to A. des Cloizeaux, these angles are, for red-light,  $2H_a = 80^\circ 26'$ ;  $2H_0 = 121^\circ 19'$ ;  $2E = 142^\circ 22'$ ; and  $2V = 73^\circ 4'$ ; for yellow-light,  $2H_a = 80^\circ 35'$ ;  $2H_0 = 121^\circ 10'$ ;  $2E = 143^\circ 14'$ ; and  $2V = 73^\circ 10'$ ; and for violet-light,  $2H_a = 80^\circ 54'$ ;  $2H_0 = 120^\circ 52'$ ;  $2E = 146^\circ 46'$ ; and  $2V = 73^\circ 26'$ . E. S. Larsen gave  $2H_0 = 90^\circ 01'$ ,  $2V_a = 83^\circ 17'$  for Na-light; N. H. Winchell,  $2V = 73^\circ 10'$ ; and V. Rosicky,  $2V = 73^\circ 71'$  to  $73^\circ 20'$ . M. Kuhara studied the tear-figures or percussion figures of vivianite.

C. F. Rammelsberg gave 2.58 to 2.68 for the sp. gr. of vivianite; S. P. Popoff, 2.66; C. Schmidt, 2.542. The observed results for the sp. gr. of vivianite range from 2.5° to 2.72. E. S. Larsen gave 2.670 to 2.693 at 18°. The mean can be taken as 2.65. V. Rosicky found 2.678 for the vivianite from Vladic, and 2.686 for that from Cornwall. T. L. Watson and S. D. Gooch gave 2.693 for the sp. gr. of vivianite from Florida. The hardness of the crystals is 1.5 to 2.0. N. S. Kurnakoff and I. A. Andreevsky found that the dehydration curve has arrests at  $110^\circ$  to  $112^\circ$ ,  $170^\circ$ ,  $296^\circ$  to  $304^\circ$ . R. Cusack gave  $1114^\circ$  for the m.p. T. L. Watson and S. D. Gooch gave for the refractive indices,  $\alpha = 1.580$ ;  $\beta = 1.598$ , and  $\gamma = 1.627$ ; E. S. Larsen gave  $\alpha = 1.579$ ,  $\beta = 1.603$ , and  $\gamma = 1.633$ ; H. Berman,  $\alpha = 1.584$ ,  $\beta = 1.600$ , and  $\gamma = 1.634$ ; N. H. Winchell,  $\alpha = 1.5766$ ,  $\beta = 1.6050$ , and  $\gamma = 1.6267$ ; and V. Rosicky,  $\alpha = 1.5809$ ,  $\beta = 1.6038$ , and  $\gamma = 1.6361$ ; F. Ulrich, T. L. Watson and S. D. Gooch, and A. Lacroix also made observations on the subject. R. Robl observed no luminescence in ultra-violet light.

Ferrous phosphate, vivianite, as indicated above, rapidly oxidizes on exposure to air, thereby losing its white colour, and, passing through deepening shades of blue, finally becoming brown beraunite, or something similar. Oxidation occurs rapidly when the mineral is finely ground. A. Gärtner analyzed vivianite in three forms—(i) freshly dug; (ii) after a month's exposure; and (iii) after three months' exposure, and found:

	MgO	CaO	FeO	Fe <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	Loss	Organic and sand	CO <sub>2</sub>
(i) . . .	—	3.69	39.76	3.07	25.82	6.64	20.02	—
(ii) . . .	0.11	2.59	25.70	6.10	17.70	35.07	9.55	—
(iii) . . .	0.09	2.40	19.55	18.11	12.02	26.05	14.48	7.3

The subject was further considered by G. Tschermak, T. L. Watson, M. Oknoff, and S. P. Popoff. The last-named considered that the stages in the oxidation of paravivianite,  $(\text{Mg,Ca,Mn,Fe})_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ , are represented  $\beta$ -kertschenite,  $\alpha$ -kertschenite, and oxykertschenite, whose graphic formulæ have been previously indicated. F. Cornu observed that moist vivianite has a strong acidic reaction. The salt is said to be insoluble in water, but F. K. Cameron and L. A. Hurst showed that the phosphates of iron, aluminium, and calcium are hydrolyzed by water which becomes more acidic, and a basic phosphate remains. S. R. Carter and N. H. Hartshorne studied the ternary system:  $\text{FeO}-\text{P}_2\text{O}_5-\text{H}_2\text{O}$ , at  $70^\circ$ , with between 7.38 and 57.51 per cent. of phosphoric acid. Within this range, the stable phases are:  $2\text{FeO} \cdot \text{P}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$ , or  $\text{FeHPO}_4 \cdot 2\text{H}_2\text{O}$ ;  $2\text{FeO} \cdot \text{P}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ , or  $\text{FeHPO}_4 \cdot \text{H}_2\text{O}$ ;

and  $\text{FeO} \cdot \text{P}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$ , or  $\text{Fe}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ . No vivianite appears. Expressing the concentration of the liquid phase in percentages, the ranges of stability of the solid phases are :

FeO . . .	2.76	4.38	5.54	7.71	9.12	11.9	10.5	6.29	3.15
$\text{P}_2\text{O}_5$ . .	7.38	12.06	15.1	21.6	24.29	36.99	38.86	46.61	57.51
	$\text{FeHPO}_4 \cdot 2\text{H}_2\text{O}$			$\text{FeHPO}_4 \cdot \text{H}_2\text{O}$			$\text{Fe}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$		

Returning to vivianite, J. I. Pierre said that 1 part of ferrous phosphate is soluble in 1000 parts of water containing more than 1 vol. of carbon dioxide. J. M. van

Bemmelen found that hydrogen dioxide also oxidizes vivianite to a product resembling beraunite. W. Kangro and R. Flügge observed that at  $900^\circ$ , chlorine gas removed 96.7 per cent. of the iron from vivianite, but no phosphorus was removed. L. Cambi and A. Cagnasso studied the absorption of nitric oxide by ferrous hydrophosphate suspended in water at  $0^\circ$ , and noted that as the nitric oxide is reduced to nitrous oxide, some hypoxynitrite is produced. W. Wardlaw and co-workers found that ferrous phosphate in conc. soln. of phosphoric acid is considerably oxidized by sulphur dioxide;  $4\text{Fe}(\text{H}_2\text{PO}_4)_2 + 4\text{H}_3\text{PO}_4 + \text{SO}_2 = 4\text{Fe}(\text{H}_2\text{PO}_4)_3 + 2\text{H}_2\text{O} + \text{S}$ .

According to E. J. Evans, ferrous phosphate is

soluble in acids, and in aq. ammonia; and, according to R. H. Brett, it dissolves in soln. of ammonium salts. F. Ephraim observed that no iron nitride is formed when sodamide is heated with ferrous phosphate. H. C. Bolton observed that it is soluble in cold citric acid; and J. I. Pierre found 1 part of ferrous phosphate is soluble in 560 parts of water containing  $\frac{1}{560}$ th part of acetic acid, and 1 part of the phosphate dissolves in 1666 parts of water containing 150 parts of ammonium acetate. J. Spiller found that the presence of sodium citrate prevents the precipitation of ferrous phosphate. According to A. Naumann, the phosphate is insoluble in acetone. Ferrous phosphate is soluble in an excess of a soln. of a ferrous salt. A boiling soln. of potassium hydroxide dissolves out the phosphoric acid from vivianite. W. Heike represented the reaction with calcium oxide:  $\text{Fe}_3(\text{PO}_4)_2 + 4\text{CaO} \rightleftharpoons \text{Ca}_4\text{P}_2\text{O}_9 + 3\text{FeO}$ .

According to M. Messini, when ferrous sulphate is intravenously injected in the animal body, it forms **colloidal ferrous phosphate**. This colloid is prepared by mixing soln. of sodium phosphate and ferrous sulphate in presence of the colloid, and the time interval between mixing and the appearance of flocculation was noted. The protective action of gelatin is observable at a concentration of 2.5 grms. per litre and reaches a maximum at 12.5 grms. per litre, thereafter remaining constant. The smaller the concentration of ferrous phosphate the greater is its stability; the colloid remains stable for an indefinitely long period at a concentration of 0.006 grm. per litre and in presence of 12.5 grms. per litre of gelatin. Similar results were obtained with ox-blood serum as the protective colloid. The protective effect is observed at a concentration of 100 c.c. per litre, and the colloid seems to be permanently stable when the concentration of ferrous phosphate is 0.006 grm. per litre and that of serum 700 c.c. per litre.

N. S. Maskelyne and F. Field described a mineral from the Wheal Jane mine, Truro, Cornwall, and they called it **ludlamite**—after A. Ludlam. The analysis corresponds with **ferrous hydroxyphosphate**,  $2\text{Fe}_3(\text{PO}_4)_2 \cdot \text{Fe}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ . N. Fukuchi found it near Shimotsuke, Japan. The basic phosphates were discussed by P. Jolibois and L. Cloutier. According to N. S. Maskelyne and F. Field, it occurs in small, green, monoclinic crystals with the axial ratios  $a : b : c = 2.2520 : 1 : 1.9819$ ,

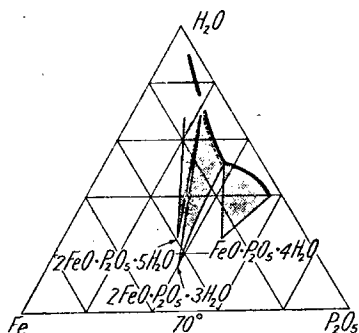


FIG. 690.—Equilibrium in the Ternary System:  $\text{FeO}-\text{P}_2\text{O}_5-\text{H}_2\text{O}$ , at  $70^\circ$ .

and  $\beta=79^\circ 27'$ . The crystals are tabular parallel to (001), and the (001)- and (111)-faces are striated or furrowed parallel to the (001)/(111)-edge. The (001)-cleavage is perfect, and the (100)-cleavage is distinct. The optic axial angles  $2H_a=97^\circ 50'$ ;  $2H_0=119^\circ$ ; and  $2V=82^\circ 22'$ ; the optical character is positive; and the dispersion is small. The sp. gr. is 3.12; and the hardness 3 to 4. H. Buttgenbach gave for the mean birefringence, 0.0142. The basic phosphate is soluble in dil. hydrochloric and sulphuric acids. F. Müllbauer obtained a hydrated ferrous hydroxyphosphate,  $\text{Fe}_7(\text{OH})_2(\text{PO}_4)_4 \cdot 5\text{H}_2\text{O}$ , with small proportions of manganese and magnesium. The mineral occurs in apple-green, monoclinic crystals from Hagendorf, Bavaria. He called the mineral **lehnerite**—after F. Lehner. H. Steinmetz gave the formula:  $\text{R}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ . The axial ratios are  $a:b:c=0.89651:1:2.4939$ , and  $\beta=110^\circ 23'$ . The basal cleavage is perfect. The mineral was discussed by H. Berman, and it is thought to be identical with ludlamite. E. S. Larsen thus compared some properties of the two minerals:

	Refractive indices			Opt. Char.	Axial Angle	Cleavage Perfect	Sp. gr.	Hardness
	$\alpha$	$\beta$	$\gamma$					
Lehnerite	1.650	1.669	1.689	+	Large	(001)	3.19	3.5
Ludlamite	1.653	1.675	1.697	+	$82^\circ$	(001)	3.12	3 to 4

A. Vogel, and J. W. Döbereiner observed that ferrous phosphate dissolves in aq. ammonia, forming a brown soln., which, on evaporation, gives up the ammonia. F. J. Otto prepared **ammonium ferrous phosphate**,  $\text{NH}_4\text{FePO}_4 \cdot \text{H}_2\text{O}$ , by mixing a soln. of iron in hot hydrochloric acid with a little ammonium sulphite, and then adding to the hot soln., a boiled aq. soln. of sodium hydrophosphate, when ferrous phosphate is precipitated. Aq. ammonia is then added in excess, and, after agitation, the flocculent precipitate is converted into tabular crystals which rapidly settle. If it be still flocculent, heat again and add more ammonia. The crystals are not now so sensitive to the oxidizing action of air, and they can be washed with thoroughly boiled water, and dried. No ammonia must be added, since its presence favours oxidation. The greenish-white, soft laminae are permanent in air, they are decomposed when heated, leaving at first ferrous phosphate, and this passes to the ferric phosphate. The salt gives off ammonia when treated with potash-lye, and if the mixture be boiled, ferrosic oxide is formed. The salt is insoluble in water, even when boiling. The freshly-prepared, moist salt is soluble even in dil. acids, but when it has been dried, it dissolves with difficulty even in conc. acids.

A. Sachs observed crusts of crystals lining cavities in the limonite mines of Zelesnyj Rog, near Anapa, on the Taman Peninsula, Kuban Province, Russia, and the mineral as a **calcium ferrous phosphate**,  $2\text{CaO} \cdot \text{FeO} \cdot \text{P}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$ , or  $(\text{Ca}, \text{Fe})_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ . It was called **anapaite**. S. P. Popoff called it **tamanite**. Analyses were made by A. Sachs, S. P. Popoff, and J. Loczka. The crystals were examined by P. N. Tschirwinsky, and C. Palache. The greenish-white mineral has triclinic crystals with the axial ratios  $a:b:c=0.8757:1:0.5975$ , and  $\alpha=132^\circ 22'$ ,  $\beta=106^\circ 47'$ , and  $\gamma=83^\circ 28'$ , according to A. Sachs;  $0.7069:1:0.8778$ , and  $\alpha=97^\circ 42'$ ,  $\beta=95^\circ 17'$ , and  $\gamma=70^\circ 11'$ , according to S. P. Popoff; and  $0.8575:1:0.9401$ , and  $\alpha=108^\circ 56' 40''$ ,  $\beta=104^\circ 05' 40''$ , and  $\gamma=78^\circ 25' 24''$ , according to C. Palache. The (100)-cleavage is perfect. The sp. gr. is 2.81 to 2.85, and the hardness 3.5.

S. G. Gordon obtained two minerals, **aluminium ferrous phosphates**, from the rhyolite at Llallagna, Oruro, in Bolivia. One called **vauxite**—after G. Vaux—has a composition corresponding with  $4\text{FeO} \cdot 2\text{Al}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5 \cdot 24\text{H}_2\text{O} + 3\text{H}_2\text{O}$ , where the  $3\text{H}_2\text{O}$  is given off at  $104^\circ$ . Another specimen gave  $\text{FeO} \cdot \text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot 6\text{H}_2\text{O}$ . The radiating aggregates of sky-blue, triclinic crystals have the axial ratios  $a:b:c=1.1510:1:1.2624$ , and  $\alpha=99^\circ 21'$ ,  $\beta=102^\circ 14'$ , and  $\gamma=110^\circ 14'$ . The optical character is positive; the refractive indices,  $\alpha=1.551$ ,  $\beta=1.555$ , and  $\gamma=1.562$ ; the hardness is 3.5; and the sp. gr. 2.375. The other mineral, called **paravauxite**, has

the composition:  $5\text{FeO} \cdot 4\text{Al}_2\text{O}_3 \cdot 5\text{P}_2\text{O}_5 \cdot 26\text{H}_2\text{O} + 21\text{H}_2\text{O}$ , where the  $21\text{H}_2\text{O}$  is lost at  $104^\circ$ . Another specimen gave  $\text{FeO} \cdot \text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$ . The colourless, prismatic, triclinic crystals have the axial ratio  $a : b : c = 0.5058 : 1 : 0.6882$ , and  $\alpha = 97^\circ 42'$ ,  $\beta = 110^\circ 22'$ , and  $\gamma = 100^\circ 56'$ . The (010)-cleavage is good; the optical character is positive; the refractive indices,  $\alpha = 1.554$ ,  $\beta = 1.558$ , and  $\gamma = 1.573$ ; the hardness is 3; and the sp. gr. 2.291. S. G. Gordon also obtained what he called **metavauxite**, in monoclinic crystals approximating  $\text{FeO} \cdot \text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$ . For **lazulite**,  $(\text{Fe}, \text{Mg})\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot \text{H}_2\text{O}$ , *vide* 5. 33, 23.

For **ferrous lithium phosphate**,  $\text{Li}_3\text{PO}_4 \cdot \text{Fe}_3(\text{PO}_4)_2$ , *vide* manganese phosphates, *triphyllite*. F. Zambonini, and B. Gossner and H. Strunz studied the isogonism of triphyllite,  $\text{LiFePO}_4$ , and olivine,  $\text{MgMgSiO}_4$ ; for **manganous ferrous phosphate**, *vide* manganese phosphates, *triphite*. O. Barbosa described a mineral, manganous ferrous phosphate—**zwieselite**—from Sao Gonçalo, Rio de Janeiro. F. Müllbauer's hydrated manganese ferrous phosphate,  $(\text{Mn}, \text{Fe}, \text{Mg})_3(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$ , or **wenzelite** was described in connection with manganous phosphates. The phosphorite **collinsite**, described by E. Poitevin, from François Lake, British Columbia, has the composition:  $\text{Ca}_2(\text{Mg}, \text{Fe})(\text{PO}_4)_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ —H. Steinmetz gave  $\text{RHPO}_4 \cdot 2\text{H}_2\text{O}$ —sp. gr. 3.04; hardness 4.5; and indices of refraction  $\alpha = 1.63$ ,  $\beta = 1.626$ , and  $\gamma = 1.629$ .

M. Websky reported a mineral to occur near Michelsdorf, Silesia, in irregular ellipsoids or distorted six-sided plates with a colour on a fresh surface varying from flesh-red to lavender-blue. It was called **sarcopside**, and it is a **ferrous manganous fluophosphate**, approximating  $2\text{R}_3(\text{PO}_4)_2 \cdot \text{RF}_2$ , where R denotes Fe, Mn, Mg, Ca. It was examined by E. F. Holden, and it is related in some respects to *triphite*,  $(\text{Fe}, \text{Mn})\text{PO}_4 \cdot (\text{Fe}, \text{Mn})\text{F}$ . This mineral was discussed by E. V. Shannon, and E. P. Henderson, who showed that the ferrous iron might range from 1.68 to 41.42 per cent. A variety rich in iron was called **zwieselite**. The sp. gr. of sarcopside is 3.64; and M. Websky gave 3.692 to 3.730; the hardness, 4; and, according to M. Websky, the refractive index is 1.700 to 1.725. The pleochroism is a yellow to yellowish-brown, and  $\beta$  light to dark olive-green. All water is expelled at  $110^\circ$ . It is soluble in dil. hydrochloric or sulphuric acid. D. Guimaraes described a phosphate of iron, manganese and other bases of the general formula:  $4\text{R}_3'\text{PO}_4 \cdot 9\text{R}_3''(\text{PO}_4)_2$ , and he called it **arrojadite**. The dark green, biaxial, monoclinic crystals have a perfect cleavage; they are pleochroic, having  $\alpha$  and  $\beta$  colourless, and  $\gamma$  pale green; the optical character is negative; the optic axial angle  $2V = 71^\circ$ ; the hardness is over 5; and the index of refraction  $\gamma = 1.70$ , and  $\gamma - \alpha = 0.007$ . It occurs at Serro Branco, Brazil, and is believed to be the same as a phosphate from South Dakota previously reported by W. P. Headden. H. Laubmann and H. Steinmetz reported a mineral, **phosphorphyllite**, to occur in colourless or pale blue, monoclinic crystals, with a perfect micaceous cleavage, at Hagendorf, Bavaria. It is a hydrated **ferrous aluminium sulphatophosphate** approximating  $3(\text{Fe}, \text{Mg}, \text{Ca}, \text{K})_3(\text{PO}_4)_2 \cdot 2\text{Al}(\text{OH})\text{SO}_4 \cdot 9\text{H}_2\text{O}$ . It was also discussed by C. Palache and H. Berman. H. Steinmetz, and H. Laubmann and H. Steinmetz described a ferrous manganous phosphate,  $(\text{Fe}, \text{Mn})_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ , occurring as cloudy white or green crystalline masses in the pegmatite at Hagendorf, Bavaria, and it was called **phosphoferrite**. The rhombic crystals have the axial ratios  $a : b : c = 0.8629 : 1 : 0.9418$ , and sp. gr. 2.96 to 3.10. The (010)-cleavage is not perfect; the optical character is negative.

H. St. C. Deville and H. Caron reported the preparation of **manganous ferrous fluophosphate**,  $(\text{Mn}, \text{Fe})_3(\text{PO}_4)_2 \cdot (\text{Mn}, \text{Fe})\text{F}_2$ , as well as of **manganous ferrous chlorophosphate**,  $(\text{Mn}, \text{Fe})_3(\text{PO}_4)_2 \cdot (\text{Mn}, \text{Fe})\text{Cl}_2$ .

According to H. Berman and F. A. Gonyer the yellowish-green, tabular crystals of *dickinsonite* have the composition:  $7(\text{Mn}, \text{Fe})\text{O} \cdot 0.2(\text{K}, \text{Na}, \text{Ca})\text{O} \cdot 3\text{P}_2\text{O}_5 \cdot \text{H}_2\text{O}$ ; *fairfieldite* has the composition:  $(\text{Mn}, \text{Fe})\text{O} \cdot 0.2\text{CaO} \cdot \text{P}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ ; *reddingite*,  $3(\text{Mn}, \text{Fe})\text{O} \cdot \text{P}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ ; *triploidite*,  $4(\text{Mn}, \text{Fe})\text{O} \cdot \text{P}_2\text{O}_5 \cdot \text{H}_2\text{O}$ ; and *lithiophilite*,  $2(\text{Mn}, \text{Fe})\text{O} \cdot \text{Li}_2\text{O} \cdot \text{P}_2\text{O}_5$ —*vide* manganese phosphates, 12. 64, 26. A. Breithaupt described a clove-brown variety of triploidite, rich in iron, as the mineral **zwieselite**,

and E. F. Glocker, as the mineral *zwieselite*. It occurs at Rabenstein, in Bavaria; and O. Barbosa described a variety from São Gonçalo, Brazil.

A. Lévy reported a yellowish-white, pale yellowish-brown, or brownish-black, crystalline mineral occurring in Cornwall and Devon. Its composition corresponds with **ferrous aluminium phosphate**,  $2\text{AlPO}_4 \cdot 2(\text{Fe}, \text{Mn})(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ , and he called it **childrenite**—after J. G. Children. Another mineral with a higher proportion of manganese, occurring in Hebron, U.S.A., was described by G. J. Brush and E. S. Dana, and named **eosphorite**—*vide* 12. 64, 26. According to A. Lévy, and J. P. Cooke, childrenite appears in six-sided pyramids belonging to the rhombic system. W. H. Miller gave for the axial ratios  $a : b : c = 0.77801 : 1 : 0.52575$ ; and A. des Cloizeaux gave for the optic axial angles  $2E = 75^\circ 22'$  for red-light,  $74^\circ 25'$  for yellow-light, and  $71^\circ 31'$  for blue-light. The cleavage (100) is imperfect; the optical character is negative; the sp. gr. is 3.18 to 3.24; and the hardness 4.5 to 5.0. Observations were made by F. Slavik, and F. Kolbeck. E. S. Larsen gave for the indices of refraction  $\alpha = 1.643$ ,  $\beta = 1.678$ , and  $\gamma = 1.684$ . Childrenite is soluble in hydrochloric acid. F. Slavik described a mineral from Ehrenfriedersdorf which he called **roscherite**—after W. Roscher. The mineral occurs in short columns or thin plates which are pleochroic,  $\alpha$  yellow with a tinge of olive-green,  $\beta$  brownish-yellow with a tinge of green, and  $\gamma$  chestnut-brown. Its composition corresponds with  $(\text{Fe}, \text{Mn}, \text{Ca})_2\text{Al}(\text{OH})(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ . The monoclinic crystals have the axial ratios  $a : b : c = 0.94 : 1 : 0.88$ , and  $\beta = 99^\circ 50'$ . The (001)-cleavage is nearly perfect, and the (010)-cleavage is distinct. The mean index of refraction is 1.625 to 1.630. The sp. gr. is 2.916, and the hardness 4.5.

C. W. Scheele found that phosphoric acid dissolves iron with the evolution of hydrogen, and the formation first of an acidic salt, and afterwards a greenish-white substance approaching the normal salt in composition. A. Vogel observed that the acid soln. gives a greenish precipitate with ammonia, and it is soluble in an excess of that reagent. H. Debray prepared **ferrous hydrophosphate**,  $\text{FeHPO}_4 \cdot \text{H}_2\text{O}$ , by dissolving iron in a boiling soln. of phosphoric acid; or by boiling a soln. of ferrous sulphate with magnesium phosphate prepared in the cold. The salt was also prepared by A. C. Becquerel. E. Erlenmeyer regarded it as impure orthophosphate, and the conditions of stability were worked out by S. R. Carter and N. H. Hartshorne, Fig. 690. The salt  $2\text{FeO} \cdot \text{P}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$  can be regarded as the *dihydrate*,  $\text{FeHPO}_4 \cdot 2\text{H}_2\text{O}$ , and the salt  $2\text{FeO} \cdot \text{P}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$  becomes the *monohydrate*,  $\text{FeHPO}_4 \cdot \text{H}_2\text{O}$ . The dotted line for the monohydrate with concentrations between 9.2 and 11.9 per cent. FeO, and 24.29 to 36.99 per cent.  $\text{P}_2\text{O}_5$ , refer to the amorphous salt. The crystalline salt appears with concentrations 7.71 to 11.29 per cent. FeO, and 21.6 to 37.21 per cent.  $\text{P}_2\text{O}_5$ . H. Debray observed that the dihydrate crystallizes in colourless needles which become blue on exposure to air. S. R. Carter and N. H. Hartshorne said that the crystals are biaxial, and positive, with an optic axial angle  $2V = 60^\circ$  to  $70^\circ$ . H. Debray said that the salt is insoluble in water. Water at  $250^\circ$  converts the salt into vivianite. The salt is readily soluble in dil. acids, and in aq. ammonia. W. Manchot found that a viscid liquid is produced when a soln. of ammonium phosphate is added to alcohol saturated with nitric oxide at  $0^\circ$ ; the oil crystallizes when placed in a freezing mixture, and when purified by re-crystallization at a low temp., brown, flaky crystals of **ferrous nitrosyl hydrophosphate**,  $\text{FeHPO}_4 \cdot \text{NO}$ , melting at  $16^\circ$ , are formed. On exposure to air, it yields white ferric phosphate. The nitrosyl complex was also studied by I. Bellucci, and E. W. Merry. R. Weinland and co-workers also prepared complexes with pyridine and methyl alcohol,  $\text{FeHPO}_4 \cdot 4\text{C}_5\text{H}_5\text{N} \cdot 2\text{CH}_3\text{OH} \cdot 4\text{H}_2\text{O}$ , and  $\text{FePO}_4 \cdot \text{FeHPO}_4 \cdot 4\text{C}_5\text{H}_5\text{N} \cdot 4\text{CH}_3\text{OH} \cdot 8\text{H}_2\text{O}$ . H. Debray prepared crystals of **ammonium ferrous hydrophosphate**,  $(\text{NH}_4)_2\text{Fe}(\text{HPO}_4)_2 \cdot 4\text{H}_2\text{O}$ , by digesting the normal salt for 7 or 8 days with a conc., acid soln. of ammonium phosphate.

E. Erlenmeyer prepared **ferrous dihydrophosphate**,  $\text{Fe}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ , by dissolving iron in an excess of phosphoric acid in a current of hydrogen to protect it



from air. The excess of acid is removed by washing with ether, and the product is dried in hydrogen. The salt is a white, crystalline powder, which readily oxidizes in air, forming a ferric salt. It is readily soluble in water, but is insoluble in alcohol. The salt is the  $\text{FeO} \cdot \text{P}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$  observed by S. R. Carter and N. H. Hartshorne, and the conditions of equilibrium at  $70^\circ$  are summarized in Fig. 690.

A. Schwarzenberg prepared **ferrous pyrophosphate**,  $\text{Fe}_2\text{P}_2\text{O}_7$ , as an unstable, white powder by the double decomposition of ferrous sulphate, and sodium pyrophosphate; or by heating ferrous orthophosphate; or by reducing ferric phosphate with hydrogen. On exposure to air, the salt turns green, and ultimately brown. The salt was also prepared by L. Ferrand. H. Struve obtained the pyrophosphate by heating the normal salt in hydrogen. H. Rose, and G. Buchner noted the precipitate is soluble in an excess of the precipitant. J. H. Gladstone found that when the soln. in dil. sulphuric acid is boiled, it deposits a precipitate of ferric pyrophosphate. C. V. Smythe found that non-ionized ferrous pyrophosphate or metaphosphate is rapidly oxidized by air regardless of the acidity of the soln., whereas ferrous sulphate in similarly acidified soln. suffered no appreciable oxidation. P. Pascal observed that a sat. soln. of ferrous pyrophosphate in one of sodium pyrophosphate slowly deposits crystals of **sodium ferrous pyrophosphate**,  $\text{Na}_3\text{Fe}_2(\text{P}_2\text{O}_7)_3$ . Solutions containing alkali ferrous pyrophosphate reduce soln. of silver and gold salts in the cold, but platinum salts are not reduced even on boiling. In the case of dil. soln., the reduced gold and silver are colloidal, and strongly coloured. Mercuric salts are reduced to mercurous salts and then to mercury; with dil. soln., the mercury is colloidal and maroon by transmitted and grey by reflected light. Soln. of cupric salts furnish colloidal, cuprous hydroxide, yellow by transmitted and green by reflected light. The yellow colour becomes darker in time, owing to the reduction of the hydroxide to metallic copper. At  $100^\circ$ , the copper is deposited on glass as a thin film. S. Freed and C. Kasper discussed the complex ion  $[\text{Fe}_2(\text{P}_2\text{O}_7)_3]^{++++}$ . J. Persoz obtained a soln. of the salt and noted that it is coloured brown by hydrogen sulphide, and is completely precipitated by ammonium sulphide. H. A. Spoehr studied the catalytic action of the salt in the oxidation of carbohydrates, and J. H. C. Smith and H. A. Spoehr, in the oxidation of soln. of potassium arsenite, and sodium sulphite. A. Rosenheim prepared **ammonium ferrous pyrophosphate**,  $(\text{NH}_4)_3[\text{Fe}(\text{OH})\text{P}_2\text{O}_7] \cdot 2\text{H}_2\text{O}$ .

A. Colani prepared **ferrous metaphosphate**,  $\text{Fe}(\text{PO}_3)_2$ , as a white, insoluble powder by the action of fused metaphosphoric acid on metallic iron, on ferrous chloride or oxalate, or, best of all, ferrous phosphate, in a gold crucible in an atm. of carbon dioxide. The product is insoluble in hydrochloric and nitric acids, but it is attacked by hot, conc. sulphuric acid—for the oxidation of the soln., *vide supra*. A. Glatzel reported a *tetrahydrate*. C. G. Lindbom prepared **ferrous trimetaphosphate**,  $\text{Fe}_3(\text{P}_3\text{O}_9)_2$ , by double decomposition with the barium salt and ferrous sulphate. The salt is slightly soluble in cold water, more easily soluble in hot water; and after ignition it is soluble in hydrochloric acid only after a prolonged boiling. A. Glatzel prepared **ferrous tetrametaphosphate**,  $\text{Fe}_2\text{P}_4\text{O}_{12} \cdot 10\text{H}_2\text{O}$ , by heating an excess of phosphoric acid with a ferrous salt or oxide so that a molten mass is obtained; and this is slowly cooled. H. Lüdert obtained gelatinous **ferrous hexametaphosphate**,  $\text{Fe}_3(\text{PO}_3)_6$ , by double decomposition between sodium hexametaphosphate and ferrous salts. These two salts may be the same chemical individuals. P. Pascal prepared **sodium ferrous metaphosphate**,  $\text{Na}_4\text{Fe}(\text{PO}_3)_6$ , by the method used for the pyrophosphate.

M. Strange prepared **sodium ferrous triphosphate**,  $\text{Na}_3\text{FeP}_3\text{O}_{10} \cdot 11\frac{1}{2}\text{H}_2\text{O}$ , by adding sodium triphosphate to a soln. of ferrous sulphate. The soln., after filtration deposits the salt in slender, silky, white needles. It is stable when dry, but in contact with water, it rapidly oxidizes and forms a brown syrup which is thought to be a basic salt. It dissolves in nitric acid, and, on warming, is converted into ferric pyrophosphate with a violent evolution of nitric oxide. It is dehydrated

only by heating to the m.p., and ferrous oxide is then deposited. Observations were made by P. Glühmann.

H. Laubmann and H. Steinmetz reported an acid ferrous phosphate,  $4\text{-}5(\text{Fe,Mg,Ca}).3\text{PO}_4\cdot\text{H}_2\text{PO}_4$ , or  $\text{H}_8\text{R}_5''(\text{PO}_4)_8$ , in the pegmatite at Hagendorf, Bavaria. It was called **phosphoferrite**.

J. J. Berzelius, C. F. Rammelsberg, G. Jenzsch, and G. C. Wittstein reported a **ferrosic phosphate** of indefinite composition to be formed during the oxidation of vivianite, or of artificial ferrous phosphate in air; and W. N. Ipatéeff and W. Nikolajeff observed that the crystals of the alleged ferrosic phosphate are green, blue, or black, according to the proportion of contained ferrous iron; and that under water, at an elevated temp. and with hydrogen under press., the ferric phosphate is partially reduced to ferrosic phosphate.

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## § 51. The Ferric Phosphates

The hydrated normal **ferric phosphates** have been reported in nature. A. Nies<sup>1</sup> described a mineral from Dünsberg, Giessen, etc., which he named **strengite**—after A. Streng. Analyses reported by A. Nies, and G. A. König correspond with the *dihydrate*,  $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ . A. Lacroix described a mineral, which he called *vilateite*, which is thought to be a manganiferous strengite. The colour of strengite is peach-blossom-red, carmine and other shades of red, and sometimes it is nearly colourless. The streak is yellowish-white. It generally occurs in globular and botryoidal forms, or aggregates with a radiated, fibrous structure, and a drusy surface. Good crystals are rare. W. Bruhns and K. Busz gave for the axial ratios of the rhombic crystals,  $a : b : c = 0.86517 : 1 : 0.98272$ . The (100)-cleavage is imperfect. The optic axial angle is nearly  $60^\circ$ . W. T. Schaller gave  $\mu_\alpha = 1.71$ ,  $\mu_\gamma = 1.735$ , and for the double refraction  $\mu_\gamma - \mu_\alpha = 0.025$ . E. S. Larsen found samples with  $\mu_\alpha = 1.697$  to  $1.730$ ;  $\mu_\beta = 1.708$  to  $1.732$ ; and  $\mu_\gamma = 1.722$  to  $1.762$ ; and the pleochroism,  $\alpha$  pale violet,  $\beta$  violet, and  $\gamma$  deep blue. According to A. Nies, and A. Lacroix, the sp. gr. is 2.87; and the hardness 3 to 4. It is said to be insoluble in nitric acid, and easily soluble in hot hydrochloric acid. W. Knaust studied the coagulation of colloidal soln. of ferric hydroxide peptized with phosphoric acid.

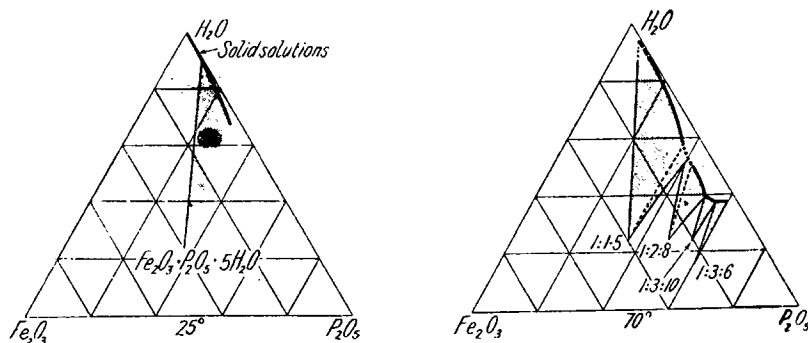
W. Bruhns and K. Busz described a mineral from Eiserfeld, Siegen, and they called it **phosphosiderite**. The analysis corresponds with the *tetritahydrate*,  $\text{FePO}_4 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ . H. Laubmann and H. Steinmetz observed that the mineral occurs at Kreuzberg. According to W. Bruhns and K. Busz, the colour of phosphosiderite is peach-blossom-red, or reddish-violet. It occurs in prismatic crystals belonging to the rhombic system, and having the axial ratios  $a : b : c = 0.53302 : 1 : 0.87723$ . The pleochroism of the crystals is distinct, since  $\alpha$  is a pale rose,  $\beta$  is carmine-red, and  $\gamma$  colourless. The (010)-cleavage is perfect. The optic axial angle is large;  $2K = 62^\circ 55'$ ;  $2E = 126^\circ 26'$ ;  $2V = 63^\circ 4'$  for yellow-light. The optical character is negative, and the index of refraction  $\beta = 1.7315$  for yellow-light. The sp. gr. is 2.76; and the hardness 3.75. It is nearly insoluble in nitric acid, but completely soluble in hydrochloric acid. It is possible by using a different orientation of the crystals to obtain the ratios  $a : b : c = 0.82285 : 1 : 0.93805$ , which is not far from strengite, but the two minerals differ in optical orientation, and chemically.

G. Cesaro described yellow, spherical aggregates of radiating needles which he called **koninckite**—after L. G. de Koninck. The mineral occurs at Richelle, Belgium. The analysis corresponds with the *trihydrate*,  $\text{FePO}_4 \cdot 3\text{H}_2\text{O}$ . The cleavage is transverse; the optical extinction parallel; the optical character positive; the optic axial angle is small; and the dispersion  $\gamma - \alpha = 0.012$ , and  $\beta - \alpha = 0.002$ . E. S. Larsen gave for the index of refraction  $\alpha = 1.645$ , and  $\gamma = 1.656$ . The sp. gr. is 2.3; and the hardness 3.5.

T. Bergman observed that when a soln. of ferric chloride is treated with sodium hydrophosphate, amorphous, yellowish-white ferric phosphate,  $\text{FePO}_4 \cdot n\text{H}_2\text{O}$ , is precipitated. E. Heydenreich obtained the precipitation, in a similar way, from soln. of ferric chloride or sulphate. H. Debray obtained it by exposing to air a soln. of iron in phosphoric acid; C. von Girsewald and H. Weidmann, by roasting ferrophosphorus; E. Erlenmeyer, by saturating with iron a 48 per cent. soln. of phosphoric acid, heated on a water-bath; R. F. Weinland and F. Ensgraber, by heating on the water-bath a mixture of ferric chloride or acetate with phosphoric acid or primary potassium phosphate; and G. Arth, by evaporating a mixed soln. of 4 mols of ferric chloride and 1 mol of sodium hydrophosphate with an excess of nitric acid—as the liquid becomes syrupy, there is a copious separation of ferric phosphate. According to F. L. Winckler, E. Heydenreich, and H. Struve, the salt precipitated from neutral soln. approximates  $\text{Fe}_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ , and, according to H. W. F. Wackenroder and C. Ludwig, and C. F. Mohr, the same substance is precipitated from an acetic acid soln., while C. R. Fresenius and H. Will said that in the presence of acetic acid, the precipitate is  $2\text{Fe}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ . R. M. Caven

recommended adding the soln. of ferric chloride to one of orthophosphoric acid prepared by boiling glacial metaphosphoric acid with water until it no longer gives a precipitate with barium chloride. The phosphoric acid, calculated as  $\text{H}_3\text{PO}_4$ , should be double the theoretical amount required to precipitate the iron. The precipitate so obtained, when suspended in water, appears perfectly white, and when strained off on calico it appears bluish-white. The washing should be done with cold water, on account of the rapid hydrolysis with hot water. F. K. Cameron and L. A. Hurst observed that it is very difficult to prepare normal ferric phosphate by the precipitation process, because, as emphasized by B. Lachowicz, the precipitate loses phosphoric acid continuously when washed by water:  $\text{FePO}_4 + 3\text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})_3 + \text{H}_3\text{PO}_4$ . The product, in consequence, contains too much or too little phosphoric acid, unless, by chance, the excess originally provided for has just been removed. This continuous hydrolysis also explains how many basic phosphates occur in nature, or have been prepared artificially. F. K. Cameron and L. A. Hurst observed no evidence of the formation of a definite basic salt. F. K. Cameron and J. M. Bell investigated the system with between 0.942 and 4.706 per cent.  $\text{P}_2\text{O}_5$  at  $25^\circ$ , and the results are in accord with the assumption that there is a continuous change in the composition of the solid phase, say  $\text{Fe}_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ , due to the adsorption of phosphoric acid. E. Erlenmeyer obtained three well-defined phosphates:  $\text{Fe}_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$ ;  $\text{Fe}_2\text{O}_3 \cdot 2\text{P}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$ ; and  $\text{Fe}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5 \cdot 6\text{H}_2\text{O}$ , as well as a series of ill-defined amorphous products with the ratio  $\text{Fe}_2\text{O}_3 : \text{P}_2\text{O}_5$  ranging from 8 : 9 to 8 : 11, and the evidence agrees with the assumption that the products are stages in a continuous process of adsorption. R. F. Weinland and F. Ensgraber observed a marked difference between the normal phosphate prepared as just indicated, and the products obtained by precipitating soln. of ferric salt with alkali phosphate soln. in the cold. The amorphous products in the latter case always varied in composition, and they contained more acid than is required for the normal salt. The subject was studied by L. Cloutier.

W. R. G. Atkins studied the effect of the acidity of the soln. on the composition of the phosphate; and S. R. Carter and N. H. Hartshorne made a partial study of



FIGS. 691 and 692.—Equilibrium Studies of the System:  $\text{Fe}_2\text{O}_3$ - $\text{P}_2\text{O}_5$ - $\text{H}_2\text{O}$ , at  $25^\circ$  and  $70^\circ$ .

the ternary system:  $\text{Fe}_2\text{O}_3$ - $\text{P}_2\text{O}_5$ - $\text{H}_2\text{O}$ , at  $25^\circ$  and at  $70^\circ$ . The results are summarized in Figs. 691 and 692. Expressing concentrations in percentage, they found:

$\text{Fe}_2\text{O}_3$	.	.	.	trace	0.23	1.40	2.43	4.42
$\text{P}_2\text{O}_5$	.	.	.	5.93	10.1	14.1	19.8	21.7
					$\underbrace{\hspace{10em}}_{\text{FePO}_4 \cdot 2\text{H}_2\text{O}}$			

The solid phase with the first mixture is  $\text{FePO}_4 \cdot n\text{H}_2\text{O} + \text{H}_3\text{PO}_4$ . This means that at  $25^\circ$ , and the lowest acid concentration, an amorphous compound,  $\text{Fe}_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ ,

is stable, and it adsorbs phosphoric acid from the mother-liquor; at higher acid concentrations another amorphous, but granular phase appears, namely, the *hemipentahydrate*,  $\text{Fe}_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$ , or  $\text{FePO}_4 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ . G. W. Waine's results agree with this. This product does not adsorb phosphoric acid. B. Ricca and P. Meduri studied the system.

Analyses of ferric phosphates were made by B. Lachowicz, P. Jolibois and L. Cloutier, M. von Wrangell and E. Koch, and F. K. Cameron and L. A. Hurst. G. C. Wittstein observed that the precipitate dried at  $50^\circ$  has the composition:  $\text{Fe}_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$ ; and when it is dried at  $100^\circ$ , C. F. Rammelsberg, A. Millot, and H. Debray found  $\text{Fe}_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$ . The product obtained by E. Erlenmeyer was represented as a *dihydrate*,  $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ , like strengite, but the analyses correspond with about  $2\frac{1}{2}\text{H}_2\text{O}$ . A. de Schulten also observed that the dihydrate is formed when 26 c.c. of a soln. of hydrated ferric chloride in half its weight of water, is heated with 4 to 5 c.c. of a soln. of phosphoric acid, of sp. gr. 1.578, in sealed tubes at  $180^\circ$  to  $190^\circ$ , for several hours; microscopic, rose-coloured crystals are obtained, which are insoluble in nitric acid, but dissolve in hydrochloric acid. If a smaller quantity of phosphoric acid is used, the crystals are much smaller; whilst if the acid is in excess, the yield is much smaller, or the liquid remains perfectly clear. In the latter case, if the proportion of phosphoric acid is not very large, crystals are still obtained by heating the tube to a higher temperature, which, however, must not exceed  $210^\circ$ , or a green basic phosphate is formed. When ferric hydroxide is heated with a soln. of phosphoric acid in sealed tubes, the product is amorphous. Unlike strengite, these crystals are monoclinic, those of strengite are rhombic. The sp. gr. is 2.74 at  $15^\circ$ ; and the crystals are birefractive, and frequently twinned. In some directions, the twins yield sections closely resembling those of rhombic strengite. R. F. Weinland and F. Ensgraber regarded their product as the hemipentahydrate. S. R. Carter and N. H. Hartshorne's results at  $70^\circ$  are summarized in Fig. 692, and expressing concentrations in percentages, they found that the solid phase with the first mixture is  $\text{FePO}_4 \cdot n\text{H}_2\text{O} + \text{H}_3\text{PO}_4$ ; and thereafter four solid phases appear:

$\text{Fe}_2\text{O}_3$	trace	< 0.1	5.45	7.12	8.10	9.79	85.8	5.28	3.46
$\text{P}_2\text{O}_5$	4.07	6.38	37.43	43.92	52.32	53.20	55.84	58.07	60.47
$\text{FePO}_4 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ $\text{Fe}_2\text{O}_3 \cdot 2\text{P}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$ $\text{Fe}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5 \cdot 10\text{H}_2\text{O}$ $\text{Fe}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5 \cdot 6\text{H}_2\text{O}$									

Accepting the analysis of the minerals strengite, phosphosiderite, and koninckite there appears to be an unknown hydrate, as well as the tri-, hemipenta-, di-, and tetraheptahydrates. R. F. Weinland and F. Ensgraber found that the water mols. of the hemipentahydrate are strongly bound. No water is lost in vacuo over sulphuric acid. The evolution of water begins at  $110^\circ$ , it comes off faster at  $120^\circ$ , and at about  $175^\circ$ , nine-tenths is lost; the remainder is expelled at  $210^\circ$ . They regard this phosphate as the ferric salt of a **hydrodiphosphatoferric acid**,  $\text{H}_3[\text{Fe}(\text{PO}_4)_2]$ , namely,  $\text{Fe}[\text{Fe}(\text{PO}_4)_2] \cdot 5\text{H}_2\text{O}$ , corresponding with a series of salts which they prepared—*vide infra*. A. Bailer's results at  $40^\circ$  are summarized in Fig. 693. He obtained the *tetrahydrate*,  $\text{H}_3[\text{Fe}(\text{PO}_4)_2] \cdot 4\text{H}_2\text{O}$ , and the *hemipenta-hydrate*,  $\text{H}_3[\text{Fe}(\text{PO}_4)_2] \cdot 2\frac{1}{2}\text{H}_2\text{O}$ , as well as **hydrotriphosphatoferric acid**,  $\text{H}_6[\text{Fe}(\text{PO}_4)_3]$ ; and the *dihydrate*,  $\text{H}_6[\text{Fe}(\text{PO}_4)_3] \cdot 2\text{H}_2\text{O}$ , as well as **hydrotetraphosphatoferric acid**,  $\text{H}_9[\text{Fe}(\text{PO}_4)_4]$ . Observations were made by A. Sanfourche and B. Focet on the complex:

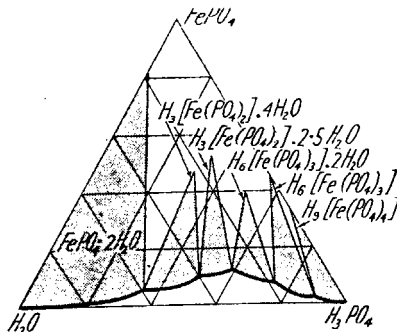


FIG. 693.—The Ternary System :  $\text{FePO}_4$ — $\text{H}_3\text{PO}_4$ — $\text{H}_2\text{O}$ .

$\text{Ca}[\text{H}_2\text{Fe}(\text{PO}_4)_2]_2$ . The subject was studied by L. Dede, who found that the conductivity curves of soln of ferric chloride and phosphoric acid in equivalent proportions gave indication of the existence of **hydrotrichloroferriphosphoric acid**,  $\text{H}_3[\text{Cl}_3\text{Fe}(\text{PO}_4)]$ , which could not be isolated, and also with more dil. soln. of  $\text{H}_3[\text{Fe}(\text{PO}_4)_2] \cdot 2.5\text{H}_2\text{O}$ .

E. Angelescu and G. Balanescu observed that well-defined ferric phosphates can be obtained only in acidic soln. According to E. A. Schneider, **colloidal ferric phosphate** is produced when a soln. of ferric chloride, saturated with normal calcium phosphate, is dialyzed. When the diffusate contained no more chloride, the ferric phosphate sol set to a jelly. The hydrogel forms a reddish-brown soln. with aq. ammonia, and ammonium phosphate is removed on dialysis. It was also prepared by E. Grimaux, and H. N. Holmes and co-workers. W. J. Sell observed that in the presence of ammonia, a soln. of ammonium hydrophosphate dissolves ferric phosphate, forming a brownish-red soln. If the soln. is dialyzed until all the electrolytes are removed, a slightly basic ferric phosphate sol is formed. The colloidal soln. of ferric phosphate is tasteless and without action on litmus. The addition of alkali chlorides and most other salts induces gelatinization. The very small value of the conductivity points to there being no free ions in the solution, and this is confirmed by the failure of potassium thiocyanate and ferrocyanide to give any colour reaction; these reagents cause gelatinization only. On the other hand, hydrogen sulphide and ammonium sulphide both give black precipitates. H. N. Holmes and R. E. Rindfusz observed the peptization of ferric phosphates by an aq. soln. of methylamine, aq. ammonia, ferric chloride, or sulphate, and nitric or hydrochloric acid. N. R. Dhar and S. Ghosh, and S. Ghosh and S. Prakash studied the subject; and A. C. Chatterji and N. R. Dhar, the rhythmic precipitation of the hydrogel. H. P. Varma and S. Prakash, and S. Prakash and N. R. Dhar found that a soln. of 0.5*M*- $\text{FeCl}_3$ , and half its vol. of 22 per cent. potassium dihydrophosphate soln. when dialyzed form a clear, red soln. S. Ghosh and co-workers studied the coagulation of the hydrosol by potassium sulphate, and by heat. The viscosities of 15 c.c. of the soln. with 46 grms. of ferric phosphate per litre and 1.2 c.c. of 0.25*N*- $\text{K}_2\text{SO}_4$ , at 30°, were:

Age . . .	0	40	80	130	185	252 mins.
Viscosity .	0.01859	0.02159	0.02648	0.03176	0.03876	0.04997

S. N. Banerji and S. Ghosh studied the viscosities of the sol at varying pressures. According to A. Arzruni, ferric phosphate is dimorphous; as just indicated, strengite is rhombic, and the artificial salt is monoclinic. The sp. gr. of the artificial dihydrate, given by A. de Schulten, is 2.74 at 15°. The action of heat on the hydrate has been indicated above. M. Faraday said that ferric phosphate is magnetic, and L. A. Welo found that the sp. magnetic susceptibility is  $71.40 \times 10^{-6}$  mass unit. L. N. Bhargava and S. Prakash studied the magnetic properties.

C. Freese observed that when ferric phosphate is heated to redness in hydrogen, ferric pyrophosphate is formed; but, according to H. Struve, if the temp. is high enough, iron phosphide,  $\text{Fe}_4\text{P}_3$ , is produced. W. Ipatéeff and W. Nikolaieff found that hydrogen above 150°, and under press., has no appreciable action on phosphoric acid and its alkali salts, but ferric phosphate under water, is partially reduced, yielding a continuous series of complex ferrosic phosphates of the type:  $\text{Fe}_n''' \text{Fe}_m'' \text{PO}_4 \cdot x\text{H}_2\text{O}$ —resembling the vivianites. T. Bergman said that 1 part of the precipitated salt is soluble in 1500 parts of boiling water, but insoluble in cold water. According to B. Lachowicz, the precipitated phosphate is only very sparingly soluble in water; but it is rapidly decomposed by contact with that liquid. The quantity hydrolyzed:  $\text{FePO}_4 + 3\text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})_3 + \text{H}_3\text{PO}_4$ , at any particular temp., depends on the amount of water present, and the decomposition does not proceed beyond a fixed limit, unless the phosphoric acid which has entered into soln. is removed from the sphere of action. In the presence of a large excess of water, the whole of the phosphoric acid is eventually drawn from

the iron phosphate. F. K. Cameron and L. A. Hurst confirmed these conclusions. They found that with a slightly acidic phosphate, after 43 days' agitation at 25°, and varying proportions of water :

Water	25	60	85	140	200	800 c.c. per gram
Dissolved PO <sub>4</sub>	0.302	0.257	0.136	0.099	0.080	0.029 grm. per litre

The phosphoric acid was still going into soln. at the end of the 43 days. The greater the proportion of water in contact with the ferric phosphate, the less is the concentration of the soln. with respect to phosphoric acid, although the total amount passing into soln. increased with increasing proportions of water. The greater the proportion of water, the less relatively is the decomposition, although actually the amount of decomposition was greater. Analogous results were obtained with a slightly basic phosphate. C. F. Mohr, and W. Hess observed that in washing the phosphate for analysis, hot water extracts phosphoric acid. Observations on the hydrolysis were also made by R. M. Caven, F. K. Cameron and L. A. Hurst, and M. von Wrangell and E. Koch; and on the gel formation, by H. L. Dube.

The presence of saline substances in water modifies its action on ferric phosphate. E. Heiden reported that the presence of sodium, potassium, and ammonium salts increases the solubility of ferric phosphate, but later work shows that this is not always the case. B. Lachowicz observed that one class of salts promotes the hydrolysis, another class retards it, whilst a third class has no action. Soln. of salts having an alkaline reaction hydrolyze the salt the more rapidly; whilst soln. of neutral salts have very little influence on the rate of hydrolysis. F. K. Cameron and L. A. Hurst found that, at 25°, with 20 c.c. of a soln. of sodium nitrate containing :

NaNO <sub>3</sub>	0	5.0	25	75	150	300 grms. per litre
Dissolved PO <sub>4</sub>	0.3500	0.2237	0.1912	0.1622	0.1451	0.1084 grm. per litre

per gram of ferric phosphate during 40 days' action; with soln. of potassium chloride :

KCl	0	0.111	5.0	25	150	300 grms. per litre
Dissolved PO <sub>4</sub>	0.3500	0.2256	0.1127	0.0905	0.0871	0.0871 grm. per litre

and with potassium sulphate during 19 days' action :

K <sub>2</sub> SO <sub>4</sub>	3	6	25	50	75	150 grms. per litre
Dissolved PO <sub>4</sub>	0.320	0.344	0.366	0.372	0.367	0.364 grm. per litre

These results obtained with a slightly acidic phosphate are similar to those obtained with a slightly basic phosphate. In these cases, the quantity of phosphoric acid in the soln. falls off rapidly as the conc. of the neutral salt is increased, or else, as in the case of the potassium sulphate soln., the phosphoric acid content increases slightly with increasing quantities of potassium sulphate in soln. The acidity increases markedly as the conc. of the neutral salt increases, and the effect is probably due to a selective adsorption whereby the basic part unites with the solid residue, leaving free acid in soln. B. Lachowicz found the following proportions of ferric oxide and phosphoric acid were dissolved from ferric phosphate by soln. of salts of this kind, during 24 hrs'. action, at 21° to 26°, using 0.5864 grm. of ferric phosphate, and a litre of soln. :

	H <sub>2</sub> O	Na <sub>2</sub> SO <sub>4</sub>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	KCl	NaCl	NH <sub>4</sub> Cl	NaNO <sub>3</sub>
Grams	—	6.761	6.364	5.624	4.410	4.029	6.464
P <sub>2</sub> O <sub>5</sub> (dissolved)	6.6	8.1	6.2	5.6	5.8	4.8	4.5 mgrms. per litre
Fe <sub>2</sub> O <sub>3</sub> (dissolved)	2.6	1.5	2.1	2.0	2.2	3.2	2.5 „ „

The action with these soln. is very little different from that of water alone; but H. Rose observed that a soln. of sodium carbonate changes the colour of ferric phosphate to reddish-brown, and phosphoric acid is dissolved. J. J. Berzelius



observed that the phosphate is soluble in a soln. of ammonium carbonate, although G. C. Wittstein said that the phosphate does not dissolve in aq. soln. of ammonium salts. Observations were also made by E. A. Schneider. B. Lachowicz's experiments were made under similar conditions to those just indicated, and gave the following results :

Grams	H <sub>2</sub> O	H <sub>2</sub> O sat. CO <sub>2</sub>	NaHCO <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub>	(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>	Ca(HCO <sub>3</sub> ) <sub>2</sub>	Na acetate
	—	—	4	5.046	2.284	1.132	6.476 per litre
P <sub>2</sub> O <sub>5</sub> dissolved	6.6	6.2	24.1	297.1	22.2	6.9	14.1 mgrms. per litre
Fe <sub>2</sub> O <sub>3</sub> dissolved	2.6	3.6	4.4	1.6	2.6	3.5	1.6 „ „

Here the salts are hydrolyzed, and the amount of phosphoric acid extracted from the ferric phosphate is much greater than is the case with water or neutral salt soln. This is also illustrated by the case of sodium hydrophosphate ; the effect is not that anticipated by the addition of a salt with a common ion, but rather that produced by a salt which hydrolyzes to form a base. This is in agreement with H. Rose's observation that ferric phosphate is immediately coloured reddish-brown by a soln. of potassium hydroxide, and the greater part of the phosphoric acid is extracted, but no ferric oxide is dissolved. Aq. ammonia behaves similarly provided no sodium phosphate forms a reddish-brown soln. with the phosphate. The ammoniacal soln. of ferric phosphate remains clear when mixed with potassium ferrocyanide, but the mixture yields prussian-blue when treated with an acid. According to J. W. Döbereiner, the salt can be separated from the ammoniacal soln. only when treated with an acid. J. B. Hester studied the base-exchange by ferric phosphate in soln. of different salts ; and S. Osugi and K. Saegi the effect of silicic acid on the solubility of ferric phosphate.

J. I. Pierre observed that 1 part of ferric phosphate dissolves in 12,500 parts of water sat. with carbon dioxide. B. Lachowicz observed that no appreciable effect on the solubility of ferric phosphate is produced by saturating the water with carbon dioxide, and this observation was confirmed by M. Gerlach who observed, further, that when calcium carbonate is mixed with either iron or aluminium phosphate in water, carbon dioxide causes an increased amount of calcium salt to pass into soln., without producing any perceptible effect on the amount of dissolved phosphoric acid. Observations were also made by M. von Wrangell and E. Koch. Calcium carbonate, and especially the hydrocarbonate, increases the solubility of ferric phosphate, and W. F. Sutherst added that while calcium carbonate has little or no influence, calcium hydroxide increases the solubility of iron and aluminium phosphates. H. J. Patterson also observed that the solubility of ferric phosphate is increased by lime. F. K. Cameron and J. M. Bell found that when 5 grms. of ferric phosphate are shaken for 5 days with 100 c.c. of :

Dissolved PO <sub>4</sub>	H <sub>2</sub> O	H <sub>2</sub> O sat. CO <sub>2</sub>	H <sub>2</sub> O sat. CaSO <sub>4</sub>	H <sub>2</sub> O sat. Ca(OH) <sub>2</sub>
	74	171	118	0 mgrms.

F. Ephraim and A. Schärer found that with gaseous hydrogen chloride, at room temp., a deliquescent addition product is formed ; and at 400°, anhydrous ferric phosphate forms a yellow powder containing about 5 mols. of HCl—it deliquesces in moist air, and is not changed by heating it to 300°. Hydrated ferric phosphate is easily soluble in dilute mineral acids, excepting phosphoric acid. R. F. Weinland and F. Ensgraber observed that, as with strengite, hydrated ferric phosphate is but slowly dissolved by nitric acid, but it is readily soluble in hydrochloric acid ; and G. Arth obtained a form which was said to be insoluble in nitric acid, but soluble in hot, conc. hydrochloric acid. A. Drevermann found that when ferric phosphate is heated with a soln. of alkali sulphide under press., iron sulphide and alkali phosphate are formed. P. Berthier showed that the freshly-precipitated salt is easily soluble in sulphuric acid, or in a soln. of ammonium sulphite, and at the same time the ferric is reduced to ferrous oxide ; and W. Wardlaw and co-workers showed that sulphur dioxide does not reduce ferric phosphate in conc. soln. of phosphoric acid.

H. Quantin observed that when ferric phosphate is heated in a current of carbon

tetrachloride, ferric chloride is formed. A. Naumann observed that ferric phosphate is insoluble in acetone. G. C. Wittstein said that ferric phosphate is insoluble in cold acetic acid; F. Sestini found that 100 c.c. of 10 per cent. acetic acid dissolves 0.007 grm. of the phosphate in the cold. The solubility of ferric phosphate in acetic acid was also discussed by G. Luff, and M. Gerlach. M. von Wrangell and E. Koch found that a litre of 0.02*N*-acetic acid dissolves 16.1 mgrms. B. Lachowicz's observations on the solvent action of sodium acetate are indicated above. T. S. Gladding, P. Cazeneuve and A. Nicolle, W. F. Sutherst, and E. Heydenreich found that the phosphate is easily soluble in tartaric and citric acids, and in the ammonium salts of these acids, and that it is also soluble in sodium citrate. J. Spiller also noted that the presence of sodium citrate prevented the precipitation of ferric phosphate. E. Erlenmeyer observed that a soln. of ammonium hydrocitrate of sp. gr. 1.09 dissolves 4.8 per cent. of  $P_2O_5$  from hydrated ferric phosphate in 35 mins.; a soln. of ammonium citrate dissolves 5.8 per cent.  $P_2O_5$ , and with an excess of ammonia, 21.2 per cent. is dissolved; whilst a 0.25 per cent. soln. of citric acid dissolves 17.5 per cent.  $P_2O_5$ . M. Gerlach observed that oxalic acid is a more effective solvent than acetic acid; in the presence of an excess of ferric hydroxide the solvent action of oxalic acid was not affected, that of citric acid was lowered, and acetic acid did not dissolve a perceptible amount of phosphoric acid.

H. J. Patterson observed that the presence of organic matter favours the hydrolytic action of water on ferric phosphate. B. Lachowicz said that the presence of humic acid increases the solubility of iron phosphate. This is based on the fact that a soln. containing sodium hydrocarbonate or ammonium carbonate and humic acid will dissolve more phosphoric acid and ferric oxide than a soln. containing carbonate alone. The effect observed, however, may have been due to the presence of free bases resulting from the hydrolysis of the humates.

Ferric phosphate is soluble in an excess of soln. of ferric salts, including ferric acetate, but it is not soluble in a soln. of ferrous acetate. E. A. Schneider examined the soln. of ferric phosphate in one of ferric sulphate. Ferric phosphate is also dissolved to a considerable extent by a soln. of ammonium humate. W. Muthmann and H. Heramhof studied the use of ferric phosphate as an underglaze colour for pottery.

As just indicated, owing to the ready hydrolysis of normal ferric phosphate it might be anticipated that a number of basic salts would have found their way into the literature of chemistry as a legacy from the days when no method was known for distinguishing the false from the true. A. F. de Fourcroy and L. N. Vauquelin,<sup>2</sup> for example, said that a polybasic salt is formed when the normal phosphate is boiled with potash-lye. The reddish-brown powder is said to be fusible. C. F. Rammelsberg obtained a similar product; and G. C. Wittstein found that it is formed when a soln. of the normal phosphate in hydrochloric acid is treated with an excess of ammonia, and the product is washed and dried. It is said to be soluble in a soln. of ammonium tartrate, but insoluble in one of ammonium citrate, and, according to A. Millot, in ammonium oxalate. G. C. Wittstein represented it as **ferric oxyphosphate**,  $2Fe_2O_3 \cdot P_2O_5 \cdot nH_2O$ . C. F. Rammelsberg as  $3Fe_2O_3 \cdot 2P_2O_5 \cdot nH_2O$ ; and A. Millot also regarded it as  $3Fe_2O_3 \cdot 2P_2O_5 \cdot 8H_2O$ . The equilibrium studies of S. R. Carter and N. H. Hartshorne, Figs. 691 and 692, do not show the existence of any such compound. Nature furnishes a few minerals which are basic salts, but that does not prove their existence as chemical individuals.

J. L. Jordan<sup>3</sup> referred to a variety of Stahlstein, and J. C. Ullmann to a Grüneisenstein, which were called by A. Brogniart, *dufrénite*—after P. A. Dufrénoy. A. Breithaupt named a variety *kraurite*—from *κραῦρος*, harsh, or dry. The mineral has been found at Anglar, Haute Vienne; at Hirschberg, Westphalia; at Rochefort en Terre, France; at St. Benigna, Bohemia; at Wheal Phoenix, Cornwall; at Allentown, New Jersey; at Rockbridge Co., Virginia; etc. Analyses were

reported by C. J. B. Karsten, C. F. Rammelsberg, C. Diesterweg, F. Kurlbaum, E. Boricky, F. Kovar and F. Slavik, H. Laubmann, E. Kinch, E. Kinch and F. H. Butler, F. A. Massie, J. L. Campbell, A. Streng, F. W. Clarke, F. Pisani, L. N. Vauquelin, and A. H. Church. The results are somewhat vague. C. F. Rammelsberg considered that specimens free from ferrous salt are best represented as **ferric trihydroxyphosphate**,  $2\text{Fe}_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ , or  $\text{Fe}_2(\text{PO}_4)(\text{OH})_3$ . This can be taken as the best representative formula, and it is in agreement with F. Kovar and F. Slavik's results; A. Streng gave  $\text{Fe}_5(\text{PO}_4)_3(\text{OH})_6$ ; and F. A. Massie gave  $4\text{Fe}_2'''(\text{OH})_3\text{PO}_4 \cdot 3\text{Fe}_2''\text{P}_2\text{O}_7$ , and E. Kinch,  $\text{FeO} \cdot 3\text{Fe}_2\text{O}_3 \cdot 2\text{P}_2\text{O}_5 \cdot 6\text{H}_2\text{O}$ .

The mineral is usually dull leek-green, olive-green, or greenish-black, and on exposure it alters to yellow or brown. The streak is siskin-green. The mineral usually occurs massive or in nodules, with a radiating fibrous structure, and drusy surface. The crystals are rare, and they are usually small and indistinct with the (001)-face rounded, and the (100)- and (010)-faces vertically striated. According to A. Streng, the rhombic crystals have the axial ratios  $a : b : c = 0.8734 : 1 : 0.4262$ . The (100)- and (010)-cleavages are indistinct. The crystals are pleochroic. The sp. gr. is 3.2 to 3.4—P. A. Dufrénoy gave 3.227. The hardness is 3.5 to 4.0. E. S. Larsen gave for the indices of refraction:  $\alpha = 1.830$ ,  $\beta = 1.840$ , and  $\gamma = 1.885$ ; and the optic axial angles:  $2V = 36^\circ$  for Na-light, and  $28^\circ$  for red-light. Dufrénite is easily soluble in hydrochloric and sulphuric acids.

A dark brown mineral found at Visé, Belgium, was named *delvauxene*—after J. C. P. Delvaux—by A. H. Dumont, and *delvauxite*, by W. Haidinger. The analyses by A. H. Dumont, and J. C. P. Delvaux correspond with  $2\text{Fe}_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot 24\text{H}_2\text{O}$ . It was also examined by A. H. Church, V. Vesely, F. Ulrich, G. Cesaro, and A. Jorissen; and a similar mineral was found at Pisek, Bohemia, by C. Vrba. G. Cesaro found pseudomorphs after gypsum. The colour is dark brown, and the sp. gr. 1.85. F. Ulrich gave 1.716 for the index of refraction with Na-light. F. Cornu, and E. Dittler have shown that the mineral is colloidal.

The mineral **beraunite** obtained by A. Breithaupt<sup>4</sup> from the vicinity of Beraun, Bohemia, has been also found in the Wheal Jane mine near Truro, Cornwall; and also at Scheibenberg, Saxony. It occurs in druses and in radiated, foliated aggregates, and as incrustations; it also occurs in monoclinic crystals. The analyses reported by C. F. Rammelsberg, G. Tschermak, H. Laubmann, E. T. Wherry, E. Boricky, A. Frenzel, and G. A. König correspond approximately with  $3\text{Fe}_2\text{O}_3 \cdot 2\text{P}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$ , which P. Groth reduced to  $\text{Fe}_3(\text{HO})_3(\text{PO}_4)_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ , or **ferric trihydroxydiphosphate**—possibly  $\text{Fe}_2\text{PO}_4(\text{OH})_3$ . G. Tschermak considered that beraunite is a product of the weathering of vivianite; and E. Boricky showed that it can also be produced from dufrénite. The mineral *eleonorite*, obtained by A. Nies from the Eleonore mine, near Giessen, was shown by A. Streng, and E. Bertrand to be identical with beraunite. The colour of beraunite is reddish-brown to dark hyacinth red, and the streak is brown. The mineral is strongly pleochroic. A. Streng gave for the axial ratios of the monoclinic crystals  $a : b : c = 2.7538 : 1 : 4.0165$ , and  $\beta = 48^\circ 33'$ . The habit of the small crystals is tabular parallel with (100), and the (100)-faces are striated parallel to the (100)/(001)-edge. Twinning occurs about the (100)-plane, and there are also penetration twins. The (100)-cleavage is distinct. G. Tschermak gave 2.95 for the sp. gr.; E. Boricky, 2.995; A. Frenzel, 2.983; and G. König, 2.940. The hardness is between 3 and 4. E. S. Larsen gave for eleonorite,  $\alpha = 1.775$ ,  $\beta = 1.786$ , and  $\gamma = 1.815$ . The mineral is soluble in hydrochloric acid.

J. Steinman described a mineral from the vicinity of St. Benigna, Bohemia, and it has been found in a few other places; it was called *kakoxen*, which has been altered to **cacoxenite**. Analyses were reported by T. Thomson, C. von Hauer, A. Streng, A. H. Church, F. von Kobell, P. A. von Holger, C. C. von Leonhard, and E. Wittich and B. Neumann. Some analyses correspond with  $2\text{Fe}_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot 12\text{H}_2\text{O}$ ; A. H. Church regarded it as a mixture of  $2\text{FePO}_4 \cdot 3\text{H}_2\text{O}$ , and  $\text{Fe}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$  with  $\text{H}_2\text{O}$ , and O. Mann also believed it to be a mixture. The mineral occurs in yellow or brownish-yellow, radiated tufts believed to be hexagonal. The sp. gr. given by A. Streng is 2.89, and E. Wittich and B. Neumann gave 2.816. The

hardness is 3 to 4. It becomes brown on exposure; and it is soluble in hydrochloric acid. H. Laubmann and H. Steinmetz observed that caxoxenite occurs in Bavaria, and another basic ferric phosphate which they called **xanthoxenite** occurs near Hübnerkobel, Bavaria.

A. Nies described a mineral which occurs amorphous, and in thin coatings in small stalactitic or spherical forms coloured dark brown. It was called **picite**, from its relationship to the picites resinacesis of A. Breithaupt. It occurs in a mine near Waldgirmes, Giessen. Analyses reported by A. Streng correspond with  $8\text{FePO}_4 \cdot 6\text{Fe}(\text{OH})_3 \cdot 27\text{H}_2\text{O}$ . A. Nies gave 2.83 for the sp. gr., and E. Boricky, 2.397. The hardness is between 3 and 4. F. Slavik said that picite is the same mineral as fouchérite—*vide infra*.

A number of acidic ferric phosphates has been reported. Some are formed by the action of conc. phosphoric acid on ferric phosphate. Thus, P. Hautefeuille and J. Margottet<sup>5</sup> said that when a soln. of ferric oxide in glacial phosphoric acid is kept over  $200^\circ$  for some time, small crystals of **ferric triorthophosphate**,  $\text{Fe}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5$ , are produced. The dark reddish-brown crystals formed at  $200^\circ$  to  $250^\circ$  appear in short, channelled, rhombic prisms; from  $250^\circ$  to incipient redness, fusiform, triclinic crystals; and at a red-heat, long, monoclinic prisms. If the temp. of formation be  $150^\circ$  to  $200^\circ$ , the **tetrahydrate**,  $\text{Fe}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$ , is formed in pinkish, nacreous, rectangular lamellæ which are not readily attacked by water or alcohol. If the temp. of formation be  $100^\circ$ , pinkish, rhombic plates of the **hexahydrate**,  $\text{Fe}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5 \cdot 6\text{H}_2\text{O}$ , are formed—*vide infra*, the dihydrophosphate; and the metaphosphate. The hexahydrate was also prepared by E. Erlenmeyer in deliquescent crystals decomposed by water into the normal phosphate; and the work of S. R. Carter and N. H. Hartshorne, Fig. 692, shows the conditions of stability of this salt.

F. L. Winckler reported that crystals of **ferric diorthophosphate**,  $\text{Fe}_2\text{O}_3 \cdot 2\text{P}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$ , or  $\text{FeH}_3(\text{PO}_4)_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ , were produced when a soln. of ferric phosphate was kept in contact with phosphoric acid for a year in a closed vessel. The excess of phosphoric acid can be removed by washing with water. The cubic, pale rose-coloured crystals were found to be insoluble in water, but furnished a red soln. with aq. ammonia, and a light brown soln. with hydrochloric acid. A. Millot found that the salt is insoluble in acetic acid; but soluble in soln. of ammonium citrate, and alkali hydroxides or carbonates. E. Erlenmeyer, L. Dede, R. F. Weinland and F. Ensgraber, and A. Millot obtained the same **octohydrate**. A. Millot said that the anhydrous salt is prepared by fusing ferric oxide with an excess of phosphoric acid, and removing the excess by washing. If a high temp. is employed, part of the product becomes insoluble in acids, but its composition is the same—*vide infra*, the dihydrophosphate. S. R. Carter and N. H. Hartshorne observed the conditions of equilibrium of the octohydrate, and also of the **decahydrate**,  $\text{Fe}_2\text{O}_3 \cdot 2\text{P}_2\text{O}_5 \cdot 10\text{H}_2\text{O}$ .

E. Erlenmeyer added that if a mol of hydrated ferric oxide be dissolved in 14 mols of  $\text{H}_3\text{PO}_4$  as 48 per cent. phosphoric acid, and the product be treated with 21 times its vol. of cold water, a greyish-yellow precipitate is formed of the composition:  $6\text{Fe}_2\text{O}_3 \cdot 7\text{P}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ , and when this is treated with boiling water,  $8\text{Fe}_2\text{O}_3 \cdot 9\text{P}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$  is formed, whilst the filtrate, when boiled, furnishes  $4\text{Fe}_2\text{O}_3 \cdot 5\text{P}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ . If alcohol be used instead of water, the white precipitate has the composition:  $8\text{Fe}_2\text{O}_3 \cdot 11\text{P}_2\text{O}_5 \cdot 9\text{H}_2\text{O}$ . C. F. Rammelsberg obtained the salt,  $2\text{Fe}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$ , in cubic crystals from a sat. soln. of the normal salt in phosphoric acid; and A. Millot, by adding water to the filtrate from  $\text{Fe}_2\text{O}_3 \cdot 2\text{P}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$ , or by heating a soln. of ferric sulphate and ammonium dihydrophosphate. E. Erlenmeyer boiled iron with an excess of phosphoric acid, and obtained a pink powder of the composition:  $4\text{Fe}_2\text{O}_3 \cdot 7\text{P}_2\text{O}_5 \cdot 9\text{H}_2\text{O}$ ; and he also prepared  $2\text{Fe}_2\text{O}_3 \cdot 5\text{P}_2\text{O}_5 \cdot 17\text{H}_2\text{O}$ , and added that a large number of compounds appear to exist between the di- and triorthophosphates. If it would serve any useful purpose, the formulæ can be arranged to make these products appear as mixed hydrophosphates. S. R. Carter and N. H. Hartshorne observed only three acidic ferric phosphates in their study of the system  $\text{Fe}_2\text{O}_3$ — $\text{P}_2\text{O}_5$ — $\text{H}_2\text{O}$ .

L. Dede found that the addition of phosphoric acid soln. to a ferric chloride soln. results in a considerable increase in the sp. conductivity of the soln.; the latter also increases rapidly with the further addition of the acid soln. and reaches a constant value when equivalent amounts of salt and acid are mixed. This is assumed to be due to the formation of the complex **trichlorophosphatoferric acid**,

$[\text{Cl}_3\text{Fe}(\text{PO}_4)_2]\text{H}_3$ . This complex acid could not be isolated; the same remark applies to its salts. A further addition of the phosphoric acid soln., whilst having no appreciable effect on the conductivity, resulted in the replacement of the three chlorine atoms of the complex by another phosphato-group, *i.e.* **diphosphatoferric acid**; this was isolated and analyzed; it corresponds with  $[\text{Fe}(\text{PO}_4)_2]\text{H}_3 + 2\frac{1}{2}\text{H}_2\text{O}$ . The complex is very stable.

According to E. Erlenmeyer,<sup>6</sup> when ferric oxide is dissolved in phosphoric acid until a precipitate begins to appear, and the soln. is then evaporated to dryness, and the excess of phosphoric acid washed out with ether, the pink, crystalline powder is **ferric dihydrophosphate**,  $\text{Fe}(\text{H}_2\text{PO}_4)_3$ . When treated with an excess of cold water it yields a yellow powder of the composition:  $8\text{Fe}_2\text{O}_3 \cdot 9\text{Fe}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ ; and with boiling water it yields normal ferric phosphate. The acidic salt:  $\text{Fe}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5 \cdot 6\text{H}_2\text{O}$ , is equivalent to this salt; whilst  $\text{Fe}_2\text{O}_3 \cdot 2\text{P}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$ , is equivalent to  $2\text{Fe}(\text{OH})(\text{H}_2\text{PO}_4) \cdot 5\text{H}_2\text{O}$ . Observations were made by R. F. Weinland and F. Ensgraber, and S. R. Carter and N. H. Hartshorne—*vide* Fig. 692; P. Hautefeuille and J. Margottet also prepared the salt in pale rose-coloured, rhombic plates. The *dihydrate*,  $\text{Fe}(\text{H}_2\text{PO}_4)_3 \cdot 2\text{H}_2\text{O}$ , was obtained by S. R. Carter and N. H. Hartshorne.

J. W. Döbereiner<sup>7</sup> observed that ferric phosphate forms a brown soln. with aq. ammonia; and, according to L. J. Cohen, when a large excess of ammonium hydrophosphate is added to a strongly acidic soln. of ferric chloride, a white precipitate of **ammonium ferric phosphate**,  $\text{NH}_4\text{H}_2\text{PO}_4 \cdot \text{FePO}_4$ , is produced. When the salt is repeatedly washed with water, it is partially hydrolyzed, and a brownish-yellow basic residue is formed. If alcohol be added to an ammoniacal soln. of the double salt, a brown gelatinous precipitate,  $2(\text{NH}_4)_2\text{HPO}_4 \cdot 3\text{FePO}_4 \cdot 3\text{Fe}(\text{OH})_3$ , is produced. R. F. Weinland and F. Ensgraber prepared **ferric amminophosphate**,  $[\text{Fe}(\text{PO}_4)_2\text{H}_3]_3\text{NH}_3 \cdot 7\text{H}_2\text{O}$ , in pink, microscopic hexagonal plates, from a mixture of 35 grms. of 85 per cent. phosphoric acid, 56 grms. of a soln. of ferric chloride (10 per cent. Fe), with a soln. of 53.5 grms. of ammonium chloride in 210 grms. of water, but allowing it to stand 6 months at ordinary temp. They also prepared the *pyridine salt*,  $\text{Fe}(\text{PO}_4)_2\text{H}_3 \cdot \text{C}_6\text{H}_5\text{N}$ . By heating on a water-bath for a prolonged period, a soln. of hydrated ferric oxide in phosphoric acid and sodium hydroxide, pale pink crystals of **sodium ferric diorthophosphate**,  $\text{NaH}_2\text{Fe}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ , are formed. This *monohydrate* gradually passes to the *trihydrate* in moist air. If a mixture of sodium chloride or phosphate and a soln. of hydrated ferric oxide in phosphoric acid is heated on a water-bath for some time, a pale pink, crystalline powder of **sodium ferric triorthophosphate**,  $\text{NaH}_2[\text{Fe}(\text{PO}_4)_3] \cdot \text{H}_2\text{O}$ , is produced. It is sparingly soluble in water. L. Ouvrard obtained by fusion the phosphate,  $3\text{Na}_2\text{O} \cdot 2\text{Fe}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5$ , which is decomposed by water; and similarly the **potassium ferric phosphate**,  $3\text{K}_2\text{O} \cdot 2\text{Fe}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5$ , which is not attacked by boiling water, and  $\text{K}_2\text{O} \cdot \text{Fe}_2\text{O}_3 \cdot 2\text{P}_2\text{O}_5$ , which is insoluble in water, and but slightly attacked by acids.

A bright green mineral was observed by J. C. Ullmann<sup>8</sup> on the dufrénite at Sayn, Westphalia, and he called it *Chalkosiderit*, *i.e.* **chalcosiderite**. The same mineral was found on the andrewsite of the West Phoenix mine, Cornwall. The analysis corresponds with **copper ferric oxyphosphate**,  $\text{CuO} \cdot 3\text{Fe}_2\text{O}_3 \cdot 2\text{P}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$ . The colour is siskin-green, and the streak pale green. The individual crystals are small, with prismatic faces, and in sheaf-like aggregates. The triclinic crystals have the axial ratios  $a : b : c = 0.7910 : 1 : 0.6051$ , and  $\alpha = 92^\circ 58'$ ,  $\beta = 93^\circ 29\frac{3}{4}'$ , and  $\gamma = 107^\circ 41'$ . The (011)-cleavage is easy; the sp. gr. is 3.108; and the hardness, 4.5. E. S. Larsen gave for the indices of refraction,  $\alpha = 1.733$  to 1.775,  $\beta = 1.840$ , and  $\gamma = 1.844$  to 1.845. Another Cornish mineral is closely related with chalcosiderite; it was called **andrewsite** by N. S. Maskelyne; the composition approximates  $5\text{Fe}_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$ , and it has 10 to 11 per cent. of copper oxide. The bluish-green, globular masses have a radiated structure, a blackish-green streak; a sp. gr. of 3.475; and a hardness of 4.

A mineral from Leoben, Styria, was called by C. von Hauer <sup>9</sup> *delvaruzene*; a specimen from Nenacovic, Bohemia, was described by E. Boricky, and called **borickite** by J. D. Dana. Analyses by C. von Hauer, and E. Boricky correspond with **calcium ferric oxyphosphate**; J. Vala and R. Helmhacker gave the formula:  $2\text{CaO} \cdot 0.5\text{Fe}_2\text{O}_3 \cdot 2\text{P}_2\text{O}_5 \cdot 16\text{H}_2\text{O}$ . C. von Hauer found that the freshly-obtained mineral, on exposure to a damp atmosphere, for:

	3	4	5	8	12 days
Gain in weight	10.06	0.36	0.12	0.23	0.01 per cent.

When the mineral is dried over calcium chloride, it loses 8.14 per cent. in 2 days, and 8.88 per cent. in 3 days. Borickite is a reddish-brown mineral gel. It occurs compact, or in reniform masses without cleavage; the sp. gr. is 2.696 to 2.707; and the hardness between 3 and 4. E. S. Larsen gave 1.57 to 1.67 for the mean refractive index. Borickite is soluble in hydrochloric acid.

J. R. Blum <sup>10</sup> described a mineral occurring in nodules in the clays of Battenberg, Rhenish Bavaria. The mineral was called **calcioferrite**. The analysis corresponds with a calcium ferric oxyphosphate,  $\text{Ca}_3\text{Fe}_2(\text{PO}_4)_4 \cdot \text{Fe}(\text{OH})_3 \cdot 8\text{H}_2\text{O}$ . The nodules or foliated masses are sulphur-yellow, greenish-yellow, siskin-yellow, or yellowish-white. The streak is sulphur-yellow. The crystal system is thought to be monoclinic. The cleavage is perfect or foliated in one direction. The sp. gr. is 2.523 to 2.529; and the hardness 2.5. A. Breithaupt <sup>11</sup> described a mineral from Schneeberg, Saxony, and Hirschberg, Westphalia, and he called it **globosite**. The analysis shows that it is a magnesium calcium ferric oxyphosphate. It occurs in wasp-yellow or yellowish-grey, globular concentrations. The sp. gr. is 2.825 to 2.827; and the hardness, 5.0 to 5.5. It is slowly soluble in hydrochloric acid. D. Guimaraes described a mineral of the wagnerite family, corresponding with  $4\text{R}_3'\text{PO}_4 \cdot 9\text{R}_3''(\text{PO}_4)_2$ , which he called **arrojadite**. It is dark green, and monoclinic, with colourless to light green pleochroism. It is biaxially negative, and has the refractive index  $\gamma = 1.70$ , and  $\gamma - \alpha = 0.007$ . The hardness is greater than 5.

V. R. von Zepharovich <sup>12</sup> obtained a mineral from Cerhovic, Bohemia, and he called it **barrandite**. Analyses reported by V. R. von Zepharovich, E. V. Shannon, and A. Lacroix correspond with **aluminium ferric oxyphosphate**,  $(\text{Fe}, \text{Al})_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$ , or  $(\text{Al}, \text{Fe})\text{PO}_4 \cdot 2\text{H}_2\text{O}$ , or, according to E. V. Shannon,  $\text{H}_2\text{Fe}(\text{PO}_5) \cdot \text{H}_2\text{O}$ . Barrandite occurs in spheroidal concretions which are indistinctly radiated and fibrous; the surface may be angular, and the structure concentric. The colour is pale bluish, reddish, greenish, or yellowish-grey; and the streak greenish to bluish-white. The sp. gr. is 2.576; the hardness, 4.5—E. V. Shannon said 2. The mean index of refraction, given by V. R. von Zepharovich, is 1.57 to 1.58—E. V. Shannon gave 1.650, and for the birefringence, 0.020; E. S. Larsen gave 0.02 for the birefringence and 1.640 for the mean refractive index. It is slowly soluble in boiling hydrochloric acid. F. Brandt described **harborite**,  $6(\text{Al}, \text{Fe})_2\text{O}_3 \cdot 4\text{P}_2\text{O}_5 \cdot 17\text{H}_2\text{O}$ , as a mineral occurring near Maranhao, Brazil. The octahedral crystals have a sp. gr. of 2.781 to 2.798; hardness of 5.0 to 5.5; and index of refraction, between 1.602 and 1.618. H. Laubmann and H. Steinmetz, <sup>13</sup> and F. Sellner described a ferric aluminium phosphate at Kreuzberg, and Königswart, and it was named **kreuzbergite**,  $(\text{Al}, \text{Fe})_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ . According to H. Laubmann and H. Steinmetz, kreuzbergite occurs in rhombic crystals with  $a:b:c = 0.3938:1:0.5261$ —F. Sellner gave  $0.42234:1:0.56194$ —its refractive index is 1.62; its birefringence 0.02 to 0.025; its sp. gr. 2.135. There is also **alumochoalcosiderite**,  $\text{CuAl}_2\text{Fe}_4(\text{PO}_4)_4(\text{OH})_8 \cdot 5\text{H}_2\text{O}$ , from Shenckenstein, described by A. Jahn and E. Gruner.

A brownish-red, amorphous mineral from Fouchère, France, was described by A. Lacroix <sup>14</sup> and called **fouchérite**—*vide* picite. Its hardness is about 3.5; and it is easily soluble in hydrochloric acid. The analysis corresponds with a **calcium aluminium ferric oxyphosphate**,  $\text{Ca}_3(\text{Fe}, \text{Al})_4(\text{PO}_4)_8 \cdot 8(\text{Fe}, \text{Al})(\text{OH})_3 \cdot 22\text{H}_2\text{O}$ .

H. Berman and F. A. Gonyer <sup>15</sup> described a mineral **landesite**,  $3\text{Fe}_2\text{O}_3 \cdot 20\text{MnO} \cdot 8\text{P}_2\text{O}_5 \cdot 27\text{H}_2\text{O}$ , *vide* manganese phosphates, 12. 64, 26. E. S. Simpson described a white, hydrated potassium aluminium ferric phosphate,  $\text{K}_2(\text{Fe}, \text{Al})_7(\text{OH})_{11}(\text{PO}_4)_4 \cdot 6\text{H}_2\text{O}$ , which he called **leucophosphate**. It is birefringent, and has a sp. gr. 2.30 to 2.65; it is insoluble in water, but soluble in conc. hydrochloric acid.

For the *manganous ferric phosphates*, *vide* manganese phosphate, 12. 64, 26.

W. T. Schaller <sup>16</sup> reported a hydrated **manganous ferric phosphate**,  $2\text{MnO} \cdot \text{Fe}_2\text{O}_3 \cdot 4\text{P}_2\text{O}_5 \cdot 14\text{H}_2\text{O}$ , to occur as a buff-coloured mineral at Pala, California. He called it **salmonsite**—after F. A. Salmon. It occurs in cleavable, fibrous masses of sp. gr. 2.85, and refractive indices  $\alpha = 1.655$ ,  $\beta = 1.660$ , and  $\gamma = 1.665$ . The optical axial angle  $2V$  is very large. The pleochroism is  $\alpha$  colourless,  $\beta$  yellow,  $\gamma$  orange-yellow. E. S. Larsen gave the refractive indices  $\alpha = 1.655$ ,  $\beta = 1.66$ , and  $\gamma = 1.670$ .

W. T. Schaller found, at Pala California, masses of a dark brown mineral which he called **sicklerite**—after the Sickler family of Pala. Its composition corresponds with a **lithium manganous ferric phosphate**,  $6\text{MnO} \cdot 3(\text{Li}, \text{H})_2\text{O} \cdot \text{Fe}_2\text{O}_3 \cdot 4\text{P}_2\text{O}_5 \cdot \text{H}_2\text{O}$ . The mineral was taken to be rhombic; the sp. gr. is 3.0; the indices of refraction  $\alpha=1.715$ ,  $\beta=1.735$ , and  $\gamma=1.745$ . The optical character is negative, and the pleochroism ranges from yellow to orange-red. E. S. Larsen gave for the indices of a variety from Utah,  $\omega=1.743$  and  $\epsilon=1.830$ .

S. L. Penfield described a mineral from Grafton, New Hampshire, and he called it **grafftonite**. Its composition approximates  $(\text{Fe}, \text{Mn}, \text{Ca})_3(\text{PO}_4)_2$ . It furnishes indistinct monoclinic crystals with lamellar intergrowths of darker-coloured triphylite. The colour is pale salmon-pink when fresh, but this becomes darker on exposure to air. Grafftonite is related to heterosite—*vide* 12. 64, 27. W. T. Schaller proposed to reserve the term heterosite for ferric phosphate and retain purpurite for manganic phosphate; but this suggestion has not been adopted. The axial ratios  $a : b : c = 0.886 : 1 : 0.582$ , and  $\beta = 66^\circ$ . The sp. gr. is 3.672, and the hardness, 5. H. Berman gave for the indices of refraction  $\alpha=1.704$ ,  $\beta=1.706$ , and  $\gamma=1.725$ . The optical character is positive, the optic axial angle  $2V=50^\circ$ ; and the dispersion is fairly strong. The mineral readily dissolves in hydrochloric acid.

G. Cesaro and G. Desprez<sup>17</sup> described a mineral from Richelle, Belgium, which they called **richellite**. The analysis corresponds with **calcium ferric fluophosphate**, although G. Cesaro gave  $8\text{Fe}(\text{PO}_4) \cdot \text{Fe}_2\text{OF}_2 \cdot (\text{OH})_2 \cdot 36\text{H}_2\text{O}$  for the formula. There was also present 5.76 to 7.19 per cent. of calcium oxide. It is yellow, and massive, compact, or foliated. The sp. gr. is 2.0, and the hardness 2 to 3. It is readily soluble in acids.

A. Breithaupt<sup>18</sup> described a yellow or yellowish-brown mineral from the alum shales of Gräfenenthal, and Saafeld, Thuringia, which was called **diadochite**—from *διάδοχος*, a successor, alluding to the hypothesis that it is an iron sinter where phosphorus has replaced the arsenic. A related mineral from Argenteau, Belgium, was called by H. Forir and A. Jorissen, **destinezite**—after M. Destinez. The analyses reported by C. F. Rammelsberg, and A. Carnot, correspond with **ferric sulphatophosphate**,  $7\text{Fe}_2\text{O}_3 \cdot 6\text{SO}_3 \cdot 3\text{P}_2\text{O}_5 \cdot 12\text{H}_2\text{O}$ ; and G. Cesaro gave for destinezite,  $2\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot \text{P}_2\text{O}_5 \cdot 12\text{H}_2\text{O}$ . The mineral occurs in reniform or stalactitic masses with a curved, lamellar structure; or else in microscopic, six-sided plates belonging to the monoclinic system. The colour is yellow or yellowish-brown. The sp. gr. is 2.035 to 2.220; and the hardness, 3. It is soluble in hydrochloric acid. F. Ulrich gave 1.815 to 1.999 for the sp. gr., 2.5 for the hardness, and 1.706 for the index of refraction for Na-light.

There is a mineral called **corkite** by M. Adam,<sup>19</sup> since it came from the Glenore mine, Cork, in Ireland; **dernbachite**, since it came from Dernbach in Nassau; and the name **beudantite** was applied by A. Lévy to the mineral from Horhausen. The analyses of F. Sandberger, C. F. Rammelsberg, and J. Percy correspond approximately with the doubtful formula:  $\text{PbSO}_4 \cdot \text{FePO}_4 \cdot 2\text{Fe}(\text{OH})_3$ . The colour is dark olive-green, yellowish-green, black, or brown. The crystals are usually opaque, seldom transparent; they are usually acute rhombohedra, sometimes square rhombohedra. The crystals belong to the rhombohedral system, and, according to H. Dauber, have the axial ratio  $a : c = 1 : 1.1842$ . The (0001)-cleavage is easy; the sp. gr. 4.0 to 4.3; and the hardness 3.5 to 4.5. E. S. Larsen gave for the mean refractive index 1.930. The optical character is negative.

A. Schwarzenberg<sup>20</sup> obtained **ferric pyrophosphate**,  $\text{Fe}_4(\text{P}_2\text{O}_7)_3$ , by treating a soln. of ferric chloride with ordinary sodium phosphate, if sodium pyrophosphate is employed, normal ferric phosphate is produced, although W. E. Ridenour reported that ferric pyrophosphate can be so prepared. According to A. Schwarzenberg, ferric pyrophosphate is a soluble powder with a yellow tinge which deepens at  $100^\circ$ , but becomes paler again on cooling. L. A. Welo found the magnetic susceptibility to be  $20.7 \times 10^{-6}$  mass unit. According to A. Schwarzenberg, ferric pyrophosphate is soluble in acids, in a soln. of sodium phosphate, of ferric chloride, of ammonium carbonate, of ammonium citrate, and in aq. ammonia; but it is

insoluble in cold hydrochloric acid, acetic acid, sulphurous acid, and in soln. of ammonium chloride. If the salt be dissolved in hot hydrochloric acid, and the soln. treated with ammonia, a precipitate of a soluble form of the pyrophosphate is obtained which is soluble in acids. J. H. Gladstone also prepared the insoluble form of the pyrophosphate; and H. Timpe, a colloidal soln. with alkali carbonate as peptizing agent. H. N. Holmes and R. E. Rindfusz also obtained a red colloidal soln. with ammonium as peptizing agent. E. Oliveri-Mandala found that ferric pyrophosphate at 30°—anhydrous and enneahydrate—dissolves in  $\text{Na}_4\text{P}_2\text{O}_7$  in the fixed ratio,  $\text{Na}_4\text{P}_2\text{O}_7 : \text{Fe}_4(\text{P}_2\text{O}_7)_3 = 3 : 1$ . Expressing concentrations in mols per litre, at 30·4° :

$\text{Na}_4\text{P}_2\text{O}_7$ . . . . .	0·14	0·20	0·26	0·32	0·38
$\text{Fe}_4(\text{P}_2\text{O}_7)_3$ { Anhydrous . . . . .	0·047	0·068	0·088	0·108	0·124
Enneahydrate . . . . .	0·050	0·072	0·094	0·114	0·134

P. Pascal found for the solubility of ferric pyrophosphate in aq. ammonia at 0°, when the concentrations are expressed per 100 grms. of sat. soln. :

$\text{NH}_3$ . . . . .	0·884	1·59	3·71	4·72	5·92	8·26	10·55	15·96	18·83
$\text{Fe}_4(\text{P}_2\text{O}_7)_3$ . . . . .	5·606	9·75	14·85	15·94	14·71	13·89	7·40	2·52	0·445

E. C. Franklin and C. A. Kraus found that the pyrophosphate is insoluble in liquid ammonia; and W. H. Krug and K. P. McElroy, that it is insoluble in acetone. E. Oliveri-Mandala found that the solubility of ferric pyrophosphate in aq. soln. of sodium citrate, at 28°, when the concentrations are expressed in mols per litre, is as follows :

Na citrate . . . . .	0·2004	0·3951	0·4760	0·5289	0·6355
$\text{Fe}_4(\text{P}_2\text{O}_7)_3$ . . . . .	0·1712	0·3160	0·3704	0·4037	0·4572

T. Fleitmann and W. Henneberg, C. N. Pahl, P. Pascal, J. Persoz, and H. Rose noted that the fresh precipitate is soluble in an excess of the precipitant, owing to the formation of a sodium ferric salt. E. Oliveri-Mandala said that at 30·3°, the solubility of ferric pyrophosphate,  $S$  mols per litre of the sat. soln., in a soln. of sodium pyrophosphate, is as follows :

$\text{Na}_4\text{P}_2\text{O}_7$ . . . . .	0·1895	0·2106	0·2835	0·3938 mol per litre
$S$ . . . . .	0·0676	0·0741	0·0990	0·1365

H. A. Spoehr and J. H. C. Smith, and E. F. Degering and co-workers studied the catalytic oxidation of carbohydrates and related compounds, and E. J. Theriault and co-workers, that of glucose, by ferric pyrophosphate. If ferric pyrophosphate be heated with two-thirds its weight of syrupy phosphoric acid and acetone for 12 hrs. at 50°, P. Pascal, and R. F. Weinland and F. Ensgraber observed that **ferric hydropyrophosphate**,  $\text{H}_6[\text{Fe}_2(\text{P}_2\text{O}_7)_3] \cdot 7\text{H}_2\text{O}$ , is formed. P. Hautefeuille and J. Margottet said that the *hydrate*,  $\text{Fe}_2(\text{H}_2\text{P}_2\text{O}_7)_3 \cdot \text{H}_2\text{O}$ , or  $\text{Fe}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$ , is formed by rapidly heating to 150° to 200° a soln. of phosphoric acid saturated with ferric hydroxide—about 15 per cent.  $\text{Fe}(\text{OH})_3$  is required. The pale rose-red crystals are rectangular, lustrous, doubly-refracting plates which can be freed from adherent phosphoric acid by washing.

According to P. Pascal, the solubility of ferric pyrophosphate in a soln. of sodium pyrophosphate is due to the formation of a complex salt, **sodium ferric pyrophosphate**,  $3\text{Na}_4\text{P}_2\text{O}_7 \cdot \text{Fe}_4(\text{P}_2\text{O}_7)_3 \cdot 9\text{H}_2\text{O}$ , or  $\text{Na}_6\text{Fe}_2(\text{P}_2\text{O}_7)_3 \cdot 9\text{H}_2\text{O}$ , and he suggested that the salts should be called *ferripyrophosphates*, analogous to the ferricyanides. The *enneahydrate*,  $\text{Na}_6\text{Fe}_2(\text{P}_2\text{O}_7)_3 \cdot 9\text{H}_2\text{O}$ , is slowly deposited from a 15 per cent. soln. of sodium pyrophosphate sat. with ferric pyrophosphate at 30°. The salt appears as a pale violet, microcrystalline powder.

S. Freed and C. Kasper discussed the complex ion  $[\text{Fe}_2(\text{P}_2\text{O}_7)_3]^{''''''}$ , A. Rosenheim and T. Triantaphyllides obtained P. Pascal's salt,  $\text{Na}_6\text{Fe}_2(\text{P}_2\text{O}_7)_3 \cdot 9\text{H}_2\text{O}$ , as well as a pale grey salt,  $\text{Na}_3\text{Fe}_4(\text{P}_2\text{O}_7)_5 \cdot 28\text{H}_2\text{O}$ , corresponding with the salt described below. C. N. Pahl also prepared the last-named salt, as well as  $5\text{Na}_4\text{P}_2\text{O}_7 \cdot \text{Fe}_4(\text{P}_2\text{O}_7)_3 \cdot 7\text{H}_2\text{O}$ .



A. Rosenheim obtained  $\text{Na}_3[\text{Fe}(\text{OH})_2\text{P}_2\text{O}_7] \cdot 4\text{H}_2\text{O}$ ; E. Oliveri-Mandala showed that C. N. Pahl's formula for the last-named salt is wrong; it should be  $3\text{Na}_4\text{P}_2\text{O}_7 \cdot \text{Fe}_4(\text{P}_2\text{O}_7)_3 \cdot 14\text{H}_2\text{O}$ . It is best prepared by saturating a soln. of sodium pyrophosphate with moist ferric pyrophosphate, by mechanical agitation; the dissolution of the calculated amount of sodium pyrophosphate in a soln. of ferric chloride of sp. gr. 1.280 to 1.282, followed by the precipitation of the double salt by alcohol gives a product contaminated with sodium chloride, and in the presence of sodium chloride the solubility determinations are too low. Ferric pyrophosphate dissolves in soln. of sodium pyrophosphate always in the proportion  $\text{Fe}_4(\text{P}_2\text{O}_7)_3 \cdot 3\text{Na}_4\text{P}_2\text{O}_7$ , independently of the concentration of the soln. Thus, expressing concentrations in mols per litre, aq. soln. of sodium citrate containing 0.3456, 0.4760, and 0.5374 mols of sodium citrate per litre, at  $26.5^\circ$ , dissolve respectively 0.0186, 0.0249, and 0.0269 mols of  $3\text{Na}_4\text{P}_2\text{O}_7 \cdot \text{Fe}_4(\text{P}_2\text{O}_7)_3$  per litre; and with soln. of sodium chloride:

NaCl	.	.	.	0.0	0.01	0.02	0.03	0.04	0.05	0.06
$\text{Na}_{12}\text{Fe}_4(\text{P}_2\text{O}_7)_6$	{	$30^\circ$	.	0.0100	0.0077	0.0053	0.0037	0.0028	0.0023	0.0020
		$50.5^\circ$	.	0.062	0.039	0.023	0.015	0.011	0.009	0.009

According to S. M. Jörgensen, when a mixture of microcosmic salt and ferric oxide is melted in a platinum dish over a Bunsen flame, and the resulting brown glass is treated with dil. hydrochloric acid to wash out the sodium phosphate, a bluish, pearly, crystalline mass of sodium ferric pyrophosphate,  $\text{NaFeP}_2\text{O}_7$ , is formed in rhombic plates, and in prisms terminated by acute pyramids. The salt is decomposed by fusion with sodium carbonate; by boiling, conc. sulphuric acid; whilst conc. hydrochloric or nitric acids have scarcely any action on the salt.

T. Fleitmann and W. Henneberg prepared sodium ferric pyrophosphate by boiling ferric pyrophosphate in excess with a soln. of sodium pyrophosphate, and precipitation with alcohol. W. H. Milck used an analogous process. Analyses of the salt were made by T. Fleitmann and W. Henneberg, J. H. Gladstone, J. Persoz, and W. H. Milck. The best representative value is:  $2\text{Na}_4\text{P}_2\text{O}_7 \cdot \text{Fe}_4(\text{P}_2\text{O}_7)_3 \cdot 14\text{H}_2\text{O}$ . The salt obtained by precipitation is colourless and easily soluble. The soln. can be evaporated to a syrupy consistency without becoming turbid, but it is thereby partially decomposed. A. Naumann observed that the complex salt is insoluble in acetone. According to W. H. Milck, no turbidity or discoloration appears if the aq. soln. be left to evaporate spontaneously for a month. When treated with hydrogen sulphide, the soln. becomes brown, and deposits sulphur; with ammonium sulphide, a green colour develops. Sodium chloride precipitates the salt from its soln.; ferric chloride precipitates ferric pyrophosphate; acids precipitate white ferric phosphate; potassium thiocyanate gives a white jelly soluble in excess. M. Rieckher said that the soln. is not precipitated by ammonium carbonate, alkali hydrocarbonates, potassium thiocyanate, sodium phosphate, or alkali acetates or succinates; freshly-precipitated barium carbonate does not precipitate ferric oxide. The soln. is not reduced by metallic iron, but it is by stannous chloride which also produces a white precipitate. W. H. Milck added that with ammonia, the soln. acquires a reddish colour, and if the boiling soln. be then evaporated, a red precipitate appears, which is soluble in ammonia, and on adding alcohol to the soln., a triple salt is deposited.

S. Frommer and W. Händler prepared **sodium ferric hydroxypyrophosphate**,  $\text{Na}[\text{Fe}(\text{OH})(\text{P}_2\text{O}_7)] \cdot n\text{H}_2\text{O}$ , as a *pentahydrate*, and *hemitrihydrate*; also **sodium ferric dihydroxypyrophosphate**,  $\text{Na}_3[\text{Fe}(\text{OH})_2(\text{P}_2\text{O}_7)] \cdot 4\text{H}_2\text{O}$ , but not the potassium and ammonium salts. They also prepared **sodium ferric pyrophosphate**,  $\text{Na}_2[\text{Fe}(\text{P}_2\text{O}_7)] \cdot 2\frac{1}{2}\text{H}_2\text{O}$ , and **ammonium ferric pyrophosphate**,  $(\text{NH}_4)_2\text{Fe}(\text{P}_2\text{O}_7) \cdot 2\text{H}_2\text{O}$ . P. Pascal emphasized the masking of the iron in sodium ferric pyrophosphate so that the soln. is simply coloured reddish-yellow when ammonia is added. When ammonia, of sp. gr. 0.880, is added to a soln. obtained by mixing 15 per cent. soln. of ferric chloride and sodium pyrophosphate, the liquid is coloured red, and

there are produced (i) a crystalline precipitate equal to one-third of the sodium pyrophosphate used ; (ii) a layer of red clots surmounted by one of yellow clots at the junction where the two liquids initially separate ; and (iii) long, silky, felted needles in the upper part of the liquid. All three products are **sodium ferric amminopyrophosphates** in which the iron is masked in the presence of the usual reagents for the detection of ferric salts. The amines are not well-defined. P. Pascal observed that when the soln. of the sodium salt,  $\text{Na}_6\text{Fe}_2(\text{P}_2\text{O}_7)_3 \cdot 9\text{H}_2\text{O}$ , is treated with a soln. of a copper salt, greenish-blue **copper ferric pyrophosphate**,  $\text{Cu}_3\text{Fe}_2(\text{P}_2\text{O}_7)_3 \cdot 12\text{H}_2\text{O}$ , and with a soln. of a silver salt, greenish-yellow **silver ferric pyrophosphate**,  $\text{Ag}_6\text{Fe}_2(\text{P}_2\text{O}_7)_3 \cdot 4\text{H}_2\text{O}$ , are formed.

The acidic salt,  $\text{Fe}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5$ , prepared by P. Hautefeuille and J. Margottet, can be regarded not only as the dihydrophosphate, but also as **ferric trimetaphosphate**,  $\text{Fe}(\text{PO}_3)_3$  ; the other two hydrates become respectively the *trihydrate*,  $\text{Fe}(\text{PO}_3)_3 \cdot 3\text{H}_2\text{O}$ , and the *dihydrate*,  $\text{Fe}(\text{PO}_3)_3 \cdot 2\text{H}_2\text{O}$ . R. Maddrell<sup>21</sup> first prepared the salt by adding ferric chloride to an excess of a dil. soln. of metaphosphoric acid, concentrating the liquid, and heating the residue to  $315^\circ$ . P. Hautefeuille and J. Margottet obtained it from a sat. soln. of ferric oxide or phosphate in metaphosphoric acid ; and K. R. Johnson, from a soln. of anhydrous ferric sulphate in that acid when the mixture is heated until crystallization sets in. The salt has a sp. gr. 3.02. It is insoluble in water, and dil. acids, but soluble in conc. sulphuric acid. P. Pascal found that **sodium ferric metaphosphate**,  $\text{Na}_3\text{Fe}(\text{PO}_3)_3$ , can be prepared from a soln. of sodium and ferric metaphosphates. P. Hautefeuille and J. Margottet obtained **silver ferric metaphosphate**,  $2\text{Ag}_2\text{O} \cdot 0.2\text{Fe}_2\text{O}_3 \cdot 5\text{P}_2\text{O}_5$ , in high refractive, rose-coloured prisms, from a fused mixture of silver phosphate and ferric metaphosphate. S. Freed and C. Kasper discussed the complex ion,  $[\text{Fe}(\text{PO}_3)_6]^{3-}$ .

A. Glatzel obtained **ferric tetrametaphosphate** by melting a ferrous or a ferric salt with a small excess of phosphoric acid, and slowly cooling the product. The violet crystals are insoluble in water, and hydrochloric or nitric acid ; they are partly decomposed by sulphuric acid. H. Lüder reported that **ferric hexametaphosphate** is not produced when sodium hexametaphosphate is treated with ferric chloride.

M. Stange<sup>22</sup> was unable to prepare **sodium ferric triphosphate**, analogous with the corresponding ferrous salt,  $\text{Na}_3\text{FeP}_3\text{O}_{10} \cdot 11\frac{1}{2}\text{H}_2\text{O}$ .

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## CHAPTER LXVII

### COBALT

#### § 1. The History of Cobalt

THE terms *kobalt*, *kobold*, *kobald*, *kobelt*, *kobolt*, *cobel*, *cobelt*, *cobalt*, etc., appear in the mining and mineralogical literature of the sixteenth century. G. Agricola,<sup>1</sup> in 1530, first used the term *kobelt* for a mineral, although, according to V. Ducange, the term was employed in 1335, in some chronicles of Leoben, for the gnomes living in the mines. *Kobold* is the German word for gnomes and goblins, and it is applied by the miners to the ore partly on account of the worthlessness of the ore, and partly on account of its mischievous effects on their own health owing to the arsenic also present in the ore. The suffering was attributed to the work of malevolent gnomes. Later, the term was extended to include the disagreeable ore. Thus, C. Encelius, in 1551, said that the name was used for a pyritic ore, and also for a metal. Similarly with G. Dorneus, M. Ruland, J. K. G. Jacobsen, D. I. Walchin, and W. Johnson. J. Mathesius, in 1562, in a series of mining sermons, wrote :

Sometimes, however, from dry, hard veins a certain black, greenish, grey or ash-coloured earth is dug out often containing good ore, and this mineral being burnt gives strong fumes and is extracted like "tutty." It is called *cadmia fossilis*. You miners call it *cobelt*. Germans call it the Black Devil and the old Devil's furies, old and black *cobel*, who injure people and their cattle with their witchcrafts. Now the Devil is a wicked, malicious spirit, who shoots his poisoned darts into the hearts of men, as sorcerers and witches shoot at the limbs of cattle and men, and work much evil and mischief with *cobalt* or *hipomane* or horses' poison. After quicksilver and *rothgültigen* ore, are *cobalt* and *wismuth* fumes; these are the most poisonous of the metals, and with them one can kill flies, mice, cattle, birds, and men. So, fresh *cobalt* and *kisswasser* [vitriol] devour the hands and feet of miners, and the dust and fumes of *cobalt* kill many mining people and workpeople who do much work among the fumes of the smelters. Whether or not the Devil and his hellish crew gave their name to *cobelt*, or *kobelt*, nevertheless, *cobelt* is a poisonous and injurious metal even if it contains silver. I find in 1 Kings 9, the word *Cabul*. When Solomon presented twenty towns in Galilee to the King of Tyre, Hiram visited them first, and would not have them, and said the land was well named *Cabul* as Joshua had christened it. It is certain from Joshua that these twenty towns lay in the Kingdom of Aser, not far from our *Sarepta*, and that there had been iron and copper mines there, as Moses says in another place. Inasmuch, then, as these twenty places were mining towns, and *cobelt* is a metal, it appears quite likely that the mineral took its name from the land of Cabul. History and circumstances bear out the theory that Hiram was an excellent and experienced miner, who obtained much gold from Ophir, with which he honoured Solomon. Therefore, the Great King wished to show his gratitude to his good neighbour by bestowing on him a number of mining towns. But because the King of Tyre was skilled in mines, he first inspected the new mines, and saw that they only produced poor metal and much wild *cobelt* ore, therefore he preferred to find his gold by digging the gold and silver in India, rather than by getting it by the *cobelt* veins and ore. For truly, *cobelt* ores are injurious, and are usually so embedded in other ores that they rob them in the fire and consume (*madtet und frisst*) much lead before the silver is extracted, and when this happens it is especially *speysig*. Therefore Hiram made a good reckoning as to the mines and would not undertake all the expense of working and smelting, and so returned Solomon the twenty towns.

In 1783, J. C. Adelung said that the metallurgists applied the term cobalt to ores—called *false ores*—which gave no metal when smelted; and in 1773, J. G. Krünitz

added that the miners applied the term *kobalt* or *kobolt* to all earths they did not know, and that later, the term was applied to earths which coloured glass blue.

The term *cobalt* or *kobold* is said to be derived from the Greek *κόβαλος*, a mine. M. Berthelot suggested that the word is of Grecian or Egyptian origin; and E. Merck derived it from the slavonic *kowalti*, metallic. W. W. Skeat, and J. Berenedes, thought that the word might have come from the Greek *κόβαλος*, a parasite, because the cobalt is usually associated with nickel; but this cannot be right, since nickel was not discovered until three centuries after the word cobalt had been in use. It is more probable that the word is of Germanic origin, and has nothing to do with Latin or Greek. The term *kobold*, at first employed locally by the miners in the Harz or Erzgebirge, became common German, and then passed into all the European languages—*vide* nickel.

According to L. Franchet, cobaltiferous earth was used by the Egyptians for colouring certain statuettes blue. The inscriptions of these figures show that they belonged to the 22nd Dynasty—about 3000 years ago. According to H. V. Hilprecht, and E. Darmstaedter, cobalt was also used for decorating pottery by the early Persians, Babylonians, Assyrians, Arabians, and the Chinese. According to B. Neumann, the ancient glasses and the glazes and bodies of many of the early Egyptian figures are coloured with copper—6. 40, 25—but, according to L. Franchet, a bluish-black cobalt colour was also employed. B. Neumann said that the glazes on the Alexandrian, Roman, and Byzantine ware which he examined owe their blue colour to copper, and not cobalt.

J. F. Gmelin, H. D. Richmond and H. Off, and M. H. Klaproth could not detect the presence of cobalt in antique glasses, but H. Davy, J. J. Ferber, J. B. J. Fourier, and X. Landerer found samples of cobaltiferous blue glass in the ruins of Pompeii, etc.; and B. Neumann observed cobalt in some ancient Venetian glasses.

The early alchemists prepared the cobalt pigment by roasting the natural mineral so as to eliminate sulphur and arsenic, and they called the product *safre*. This is not to be confounded with *azur*, which Pliny, in his *Historia naturalis* (33. 517), tells us was a blue enamel obtained by fusing cupriferous minerals with a flux. Later the term *azur* was also applied to a blue derived from cobalt as well as from copper, for P. J. Macquer said in 1789:

The vitreous glass obtained by fusing a cobalt ore with a flux is called *smalt* when it is *en masse*, and in commerce it takes the name *azur* when it has been reduced *en poudre*.

C. Piccolpassi used roasted cobalt ore for decorating pottery about 1548, and he said that the *safre* which comes from Venice, gives a brownish-violet colour. C. Piccolpassi also applied the term *bleu azur* generally to cobalt blues. In the first half of the sixteenth century, some special earths were employed for colouring glass blue. They were prepared by mixing roasted cobalt earth with sand, and different names—*sapphire*, *zaphara*, *zaphera*, *zapher*, *zaffre*, *saffra*, *safflor*, and *saffran*—were applied to the preparations by H. Cardanus, A. Cæsalpinus, J. B. Porta, and A. Libavius. Clear directions were given by J. von Kunckel, in 1679, for the preparation of *zaffre* by heating the roasted mineral mixed with sand, and of *smalt*, by fusing the mineral with sand. The history of the subject was discussed by J. C. Scaliger, C. Melzer, A. Neri, C. Merret, J. von Kunckel, W. Bruchmüller, H. Kopp, F. Kapff, and B. Neumann.

In 1540, V. Biringucci mentioned the use of *zaffera* as a mineral which does not melt alone, but which, when mixed with vitreifiable substances, melts to form an azure-blue pigment for staining glass, or pottery glazes, blue. He did not connect *zaffera* with the ores then called cobalt. G. Agricola referred to cobalt-blue, but he also missed the relation between cobalt ore and *zaffre*, for he considered that the *zaffre* came from the bismuth ore. This belief was based on the fact that the cobalt ore of Erzgebirge occurs in intimate association with bismuth ore. G. Agricola also said that "the slag of bismuth, mixed with metalliferous substances, which when melted make a kind of glass, which tint glass and earthenware glazes blue."

G. Agricola, and others indicated above, indeed, were much confused as to the zinc, cobalt, and arsenic minerals, so that cadmia and cobalt were considered to be similar things.

In the sixteenth or seventeenth century, Basil Valentine<sup>2</sup> included cobalt in a list of metallic ores; and in the sixteenth century, Paracelsus stated that a metal is produced from cobalt "which is fluid like zinc, with a peculiar black colour, beyond that of lead and iron, and possessing no brightness or metallic lustre. It is capable of being wrought, and is malleable, but not to such an extent as to fit it for practical use." There is, however, nothing here to show that Paracelsus referred to the metal now understood by cobalt.

In 1742, G. Brandt<sup>3</sup> showed that the blue colour of smalt is due to the presence of cobalt, which he regarded as a demi-metal. He obtained a regulus of cobalt, which he called *cobalt rex*, by reducing the ore, and observed that it has a grey colour with a rosy tinge, and that it may be lamellar, granular, or fibrous according to the temp. employed in reducing the metal. Like iron, too, the metal is magnetic. G. Brandt showed that the metal cobalt is free from bismuth, and that in the absence of cobalt, bismuth does not colour glass blue. A soln. of bismuth in nitric acid gives a white precipitate when treated with water, but not so with a similar soln. of cobalt. G. Brandt also showed that the blue colour of smalt is not produced by iron or by arsenic, but is solely due to the presence of cobalt. In spite of this, both J. G. Lehmann, and J. F. Henckel attributed the blue coloration to the presence of iron, or of iron and arsenic. The elemental character of cobalt was subsequently established by the work of T. Bergman,<sup>4</sup> B. M. Tassaert, C. F. Bucholz, R. Kirwan, F. Kapff, J. B. Richter, L. J. Thénard, and J. L. Proust. The history of cobalt was discussed by D. F. Hehnemann, and M. E. Weeks.

In 1653, P. Borel<sup>5</sup> suggested that invisible writing could be made by using a soln. of lead acetate in place of ordinary ink; the writing to be afterwards made visible by a soln. of a sulphide. The term *atramentum sympatheticum* was applied by J. le Mort to the invisible ink, whilst N. Lemery used the term *l'encre sympathique* for the *sympathetic ink*. Salt soln. of other metals were recommended as sympathetic inks by G. Homberg in 1698; and in 1705, D. J. Walchin recommended a soln. of bismuthiferous cobalt. The invisible writing became grass-green when heated. According to J. H. Pott, the cobalt sympathetic ink was made by a German lady at the beginning of the eighteenth century, and by H. F. Teichmeyer, about 1731. J. Hellot also relates that a German artist of Stollberg showed a cobalt sympathetic ink to him. A similar ink was suggested by F. Hoffmann in 1732; and J. Hellot, in 1737, first published recipes for preparing this sympathetic ink. J. H. Pott attributed the phenomenon to the presence of a bismuth salt, but J. A. Gesner showed that the effect is not due to the bismuth, but rather to the cobalt. The subject was discussed by G. Homberg.

H. D. Richmond and H. Off<sup>6</sup> thought that they had discovered a new element in the alum of Egypt, and they called it *masrium*, from *Masr*, the Arabic name for Egypt. Nothing further developed from the alleged discovery. J. B. Richter reported a new element to be present in cobalt ores, and it was called *niccolanum*, but it was afterwards shown to be a mixture of nickel, cobalt, arsenic, and iron. W. A. Lampadius also reported a new element in these ores, and he called it *wodanium* after the mineral *wodankies*—now *gersdorffite*—in which it was found. F. Stromeyer, however, showed that the alleged new element was a mixture of nickel, arsenic, etc. The element *gnomium*, reputed by G. Krüss and F. W. Schmidt to be present in ordinary cobalt and nickel, was disproved by C. Winkler.

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## § 2. The Occurrence of Cobalt

As emphasized by K. Kraut,<sup>1</sup> cobalt is widely diffused in nature, but not abundantly. It occurs combined usually as sulphide or arsenide, or in oxidized derivatives of these compounds. According to F. W. Clarke and H. S. Washington, the relative abundance of cobalt in the igneous rocks of the earth's crust is 0.001, when that of nickel is 0.020, and that of iron is 5.01 per cent. J. H. L. Vogt

gave  $0.00n$ ; and W. Vernadsky, 0.001. A. E. Fersmann calculated 0.00029 for the percentage number of atoms in the earth's crust. W. and J. Noddack and O. Berg gave  $3 \times 10^{-6}$  for the absolute abundance of cobalt in the earth;  $3 \times 10^{-5}$  for nickel; and  $10^{-2}$  for iron. The general subject was also discussed by A. von Antropoff, E. Dittler, G. Tammann, J. L. Howe, W. D. Harkins, V. M. Goldschmidt, E. Herlinger, G. Berg, O. Hahn, W. Lindgren, P. Niggli, R. A. Sonder, H. S. Washington, and J. Joly—*vide* the occurrence of iron.

Cobalt alloyed with iron and nickel is of extra-terrestrial origin. F. Behrend and G. Berg,<sup>2</sup> E. Cohen, J. M. Davison, A. F. Foote, V. M. Goldschmidt, H. Haushofer, W. E. Hidden, J. L. Howe, J. F. John, M. H. Klaproth, H. von Klüber, S. M. Losanitsch, A. Madelung, G. P. Merrill, P. Niggli, J. and W. Noddack, W. Ramsay and L. H. Borgström, H. N. Russell, A. Ben-Saude, F. Stromeyer, W. Tassin, W. J. Taylor, G. Trottaelli, J. H. L. Vogt, M. E. Wadsworth, E. Weinschenk, and J. E. Whitfield have reported the occurrence of cobalt in meteorites. E. Cohen agrees with J. L. Smith that cobalt is present in all the meteorites that he examined. The amount varies from about 0.5 to 2.5 per cent.—according to G. Berg, and E. Herlinger, on the average, 0.07 per cent. in stoney meteorites, and 0.58 per cent. in iron meteorites. G. P. Merrill estimated that the analyses published up to 1916 showed that meteorites contained 0.07 per cent. of metallic cobalt and 0.06 per cent. cobalt oxide. J. and W. Noddack's estimates for the percentage distribution, and the relative atomic distribution with oxygen unity, are :

Earth's crust	Igneous rocks	Meteoritic iron	Troilite	Atomic distribution
$1.8 \times 10^{-5}$	$1.8 \times 10^{-4}$	$5.47 \times 10^{-3}$	$2.08 \times 10^{-3}$	$2.7 \times 10^{-3}$

In some of the earlier analyses cobalt was not specially sought for, and its presence may therefore have been overlooked. Only in a few cases has cobalt been sought and not found. V. de Luynes, J. J. Berzelius, E. Geinitz, P. G. Melikoff and L. Pissarjewsky, I. Domeyko, W. P. Blake, and H. A. Prout discussed the subject.

The spectral lines of the sun were found by G. Kirchhoff,<sup>3</sup> H. M. Vernon, F. McClean, H. A. Rowland, C. Young, C. G. Abbot, W. W. Morgan and G. Farnsworth, F. J. M. Stratton, H. von Klüber, H. N. Russell, J. and W. Noddack, S. A. Mitchell, C. E. St. John, J. N. Lockyer; J. N. Lockyer and F. E. Baxendahl, A. de Gramont, W. F. Meggers, W. S. Adams, and A. Cornu to agree with the assumption that cobalt is present in the sun. The occurrence of cobalt in stellar atmospheres has been discussed by H. von Klüber, C. H. Payne and C. P. Chase, T. Dunham, G. E. Hale and co-workers, C. D. Shane, and V. M. Goldschmidt. J. N. Lockyer and F. E. Baxendahl observed no signs of cobalt in stellar spectra.

F. Beyschlag<sup>4</sup> and co-workers estimate that the available analyses of terrestrial materials and of meteorites show that the cobalt and nickel occur in relative proportions between 1 : 8 and 1 : 20.

Cobalt ores occur in veins along with other minerals—*e.g.*, silver, bismuth, etc.—so that the cobalt is only of secondary importance; they also occur in surface concentrations of decomposition products of the weathering of basic igneous rocks—*e.g.*, serpentized dunites or peridotites. The vein occurrences occur in different kinds of rock—*e.g.*, crystalline limestone, clay-slates, conglomerates, quartzite, schists, etc. The characters of the enclosing rocks are so varied that they furnish no clue to the origin of the cobalt. It is generally supposed that the vein deposits are of thermal origin having been transported by, and deposited from, magmatic waters of considerable depth. This is confirmed by the fact that the cobaltiferous veins are nearly always in the immediate vicinity of intrusive igneous rocks—*e.g.*, the deposits of Ontario, Canada. In some cases the veins have a dual origin, having been deposited from magmatic, and meteoric waters. Surface agencies may have altered the primary ore to form secondary minerals like erythrite. The subject has been discussed by A. E. Barlow, A. P. Coleman, A. C. Dickson, R. Beck, C. W. Knight, W. G. Miller, C. E. Ellsworth, W. Campbell and C. W. Knight,

C. Palmer and E. S. Bastin, M. E. Wilson, F. Beyschlag and co-workers, V. M. Goldschmidt, G. Berg, F. Weinert, J. H. L. Vogt, P. Niggli, H. Schneiderhöhn, A. Beutell, A. Bergeat, E. Commanducci, A. M. Finlayson, J. Roth, F. Sandberger, etc. Colloidal precipitations were studied by G. Berg, N. G. Chatterji and N. R. Dhar, P. B. Sarkar and N. R. Dhar, P. Krusch, G. A. Thiel, J. H. L. Vogt, W. Vernadsky, F. Behrend, S. Imori, A. Cissarz, and F. Beyschlag.

Metallic cobalt, in traces, occurs associated with other metals. For instance, the presence of cobalt has been noted in the iron of Ovivak, Greenland, by F. Wöhler,<sup>5</sup> A. E. Nordenskjöld, E. Cohen, F. W. Clarke, K. J. V. Steenstrup, C. Benedicks, W. Eitel, J. L. Smith, A. Daubrée, R. Naukhoff, and G. Tschermak; in the platinum metals, by P. Krusch, and L. Duparc and M. Tikanowitch; and in the silver of cobalt, Ontario, by T. L. Walker.

The more important cobalt minerals are: cobaltite, linnæite, skutterudite, smaltite, cobaltiferous pyrites, glaucodote, asbolan, and erythrite. The cobalt minerals include:

**Alloclasite**,  $(\text{Fe}, \text{Co})(\text{As}, \text{Bi})\text{S}$ , with part of the cobalt replaced by iron. **Annabergite**,  $(\text{Co}, \text{Ni})_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ . **Asbolan**—see asbolite. **Asbolite**, asbolan, earthy cobalt, or wad, an impure mixture of manganese and other oxides containing variable proportions, 4.05 to 34.37 per cent.,  $\text{CoO}$ ; that from Djebel Debar approximates  $\text{CoO} \cdot 2\text{MnO}_3 \cdot 4\text{H}_2\text{O}$ . **Badenite**,  $(\text{Co}, \text{Ni}, \text{Fe})_3(\text{As}, \text{Bi})_4$ , or  $(\text{Co}, \text{Ni}, \text{Fe})_2(\text{As}, \text{Bi})_3$ . **Bieberite**,  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ . **Bismuto-smaltite**,  $\text{Co}(\text{As}, \text{Bi})_2$ —a skutterudite containing bismuth. **Bismuth skutterudite**,  $(\text{Fe}, \text{Co})(\text{As}, \text{Bi}, \text{Sb})_3$ . **Cabrerite**,  $(\text{Ni}, \text{Mg}, \text{Co})_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ . **Carrollite**,  $\text{CuCo}_2\text{S}_4$ , or  $\text{CuS} \cdot \text{Co}_2\text{S}_3$ . **Cobalt bloom**—see erythrite. **Cobalt glance**—see cobaltite. **Cobalt ochre**—see erythrite. **Cobalt pyrites**,  $(\text{Co}, \text{Fe})\text{S}_2$ —see linnæite. **Cobalt spar**,  $\text{CoCO}_3$ —see sphærocobaltite. **Cobaltite**, or cobalt glance,  $\text{CoAsS}$ , or  $\text{CoS}_2 \cdot \text{CoAs}_2$ . **Cobaltomenite**,  $\text{CoSeO}_3 \cdot 2\text{H}_2\text{O}$ . **Danaite** is a cobaltiferous and nickeliferous mispickel. **Earthy cobalt**—see asbolite. **Erythrite**, cobalt bloom, red cobalt, or cobalt ochre,  $\text{Co}_3\text{As}_2\text{O}_8 \cdot 8\text{H}_2\text{O}$ . **Ferrocobaltite**,  $\text{FeAsS} \cdot n\text{CoAsS}$ . **Forbesite**,  $\text{H}_2(\text{Ni}, \text{Co})_2(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ . **Gersdorffite**,  $(\text{Ni}, \text{Fe}, \text{Co})\text{AsS}$ . **Glaucodote**,  $(\text{Co}, \text{Fe})\text{AsS}$ . **Grey cobalt ore**—see smaltite. **Hauchecornite**,  $(\text{Ni}, \text{Co})_7(\text{S}, \text{Sb}, \text{Bi})_3$ . **Hengleinite**,  $(\text{Co}, \text{Ni}, \text{Fe})\text{S}_2$ . **Heterogenite**, a hydrated oxide of cobalt, nickel, copper iron, or manganese. **Heubachite**,  $2\text{Co}_2\text{O}_3 \cdot \text{H}_2\text{O} + \text{Co}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ , or  $3(\text{Co}, \text{Ni}, \text{Fe})_2\text{O}_3 \cdot 4\text{H}_2\text{O}$ —a hydrated oxide of cobalt, nickel, copper, iron, and manganese. **Jaipurite**,  $\text{CoS}$ . **Julienite**, a thiocyanate,  $\text{Na}_2\text{Co}(\text{SCN})_4$ . **Kerzinite**, a peat containing nickel silicate. **Keweenawite**,  $(\text{Cu}, \text{Co}, \text{Ni})_2\text{As}$ . **Koeltigite**,  $(\text{Cu}, \text{Co}, \text{Ni})_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ . **Lavendulane**, an arsenate of cobalt and copper. **Leudouxite**,  $(\text{Cu}, \text{Co}, \text{Ni})_4\text{As}$ . **Linnæite**, siegenite, or cobalt pyrites,  $\text{Co}_3\text{S}_4$  or  $\text{CoS} \cdot \text{Co}_2\text{S}_3$ , where the cobalt is replaced by more or less nickel—siegenite—and to some extent by iron and copper. **Lubeckite**,  $4\text{CuO} \cdot \frac{1}{2}\text{Co}_2\text{O}_3 \cdot \text{Mn}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$ . **Lusakite**, a cobalt bearing silicate,  $8[\text{RO} \cdot \text{Al} \cdot \text{SiO}_4]$ . **Maucherite**,  $(\text{Ni}, \text{Co})_3\text{As}_2$ , or  $(\text{Ni}, \text{Co})_4\text{As}_3$ . **Mohawkite**,  $(\text{Cu}, \text{Co}, \text{Ni})_3\text{As}$ . **Nickel skutterudite**,  $(\text{NiCo})\text{As}_3$ . **Pateraita**, an impure mineral supposed to be a cobalt molybdate. **Penroseite**,  $2\text{PbSe}_2 \cdot 3\text{CuSe} \cdot 5(\text{Ni}, \text{Co})\text{Se}_2$ , or  $\text{PbSe} \cdot \text{Cu}_2\text{Se} \cdot 3(\text{Ni}, \text{Cu})\text{Se}_2$ . **Petzite**,  $(\text{Ag}_2\text{Al}_2, \text{Fe}, \text{Co})(\text{Te}, \text{As})$ . **Polydymite**,  $(\text{Co}, \text{Ni}, \text{Fe})_4\text{S}_8$ , or  $(\text{Co}, \text{Ni}, \text{Fe})_3\text{S}_4$ . **Rammelsbergite**,  $(\text{Ni}, \text{Co})\text{As}_2$ , or  $(\text{Ni}, \text{Co}, \text{Fe})\text{As}_2$ . **Red cobalt**—see erythrite. **Remingtonite**, a hydrated cobalt carbonate. **Rhodalose**—see bieberite. **Roselite**,  $(\text{Cu}, \text{Co}, \text{Mg})_3\text{As}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$ . **Safflorite**,  $(\text{Fe}, \text{Co})\text{As}_2$ . **Schulzenite**,  $2\text{CoO} \cdot \text{Co}_2\text{O}_3 \cdot \text{CuO} \cdot 4\text{H}_2\text{O}$ . **Siegenite**—see linnæite. **Saynite**—a polydymite. **Skutterudite**,  $\text{CoAs}_3$ . **Smaltite**, or grey cobalt ore, or speiss cobalt,  $\text{CoAs}_2$ . **Sphærocobaltite**, or cobalt spar,  $\text{CoCO}_3$ . **Speiss cobalt**,  $\text{CoAs}_2$ —see smaltite. **Stainerite**,  $(\text{Co}, \text{Al}, \text{Fe})_2\text{O}_3 \cdot \text{H}_2\text{O}$ . **Sychnodymite**,  $(\text{Co}, \text{Cu})_2\text{S}_3$ . **Tilkerodite**, a lead selenide. **Transvaalite**,  $\text{Co}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ —an oxidation product of cobalt arsenide. **Villamaninite**,  $(\text{Cu}, \text{Ni}, \text{Co}, \text{Fe})(\text{S}, \text{Se})_2$ . **Violarite**,  $(\text{Ni}, \text{Fe}, \text{Co})_3\text{S}_4$ . **Wad**—see asbolite. **Willyamite**,  $\text{CoS}_2 \cdot \text{NiS}_2$ .  $\text{CoSb}_2 \cdot \text{NiSb}_2$ , or  $(\text{Co}, \text{Ni})\text{S}_2 \cdot (\text{Co}, \text{Ni})\text{Sb}_2$ , or  $(\text{Co}, \text{Ni})\text{SbS}$ . **Winklerite**,  $2\text{Co}_2\text{O}_3 \cdot \text{Ni}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ —see heterogenite.

The ores of cobalt are not abundantly distributed.<sup>6</sup> The only deposits suitable for working under present economic conditions are those of Ontario, Missouri, New Caledonia, Belgian Congo, and Schneeberg. There are other deposits in Australia, Austria, Norway, and Sweden which have been worked. Those at Schneeberg, and Annaberg have been worked for 300 years, though the output is now very small. New Caledonia was the main source of the world's supply for some years preceding the opening up of the Ontario deposits, but the production there is now comparatively small. The map, Fig. 1, summarizes the geographical distribution of the principal deposits of cobalt.

**Europe.** In the British Isles,<sup>7</sup> a number of small and unimportant deposits of cobalt minerals has been reported—Moel Hiraddug in Flintshire; Alderley Edge and Mottram

St. Andrews in Cheshire; Wheal Trägo, Wheal Sparnon, Wheal Huckworthy, Wheal Ann, St. Austell, Fowey Consols, and East Pool in Cornwall and Devon; Hilderstone mine in Linlithgowshire; Coille-Chraghad mine in Inverary; Tyndrum mine, Argyllshire; Alva mines of Clackmannanshire; and at Corrycharmaig, Perthshire. In France,<sup>8</sup> some cobalt occurs in the silver-cobalt-nickel veins at Chalanches, Dauphiné; at Juzet, Haute-Garonne; and Sainte Marie aux Mines, Alsace. In Germany,<sup>9</sup> there are lodes at Schneeberg, and Annaberg, Saxony; and at Marienberg, Erzgebirge, Wittichenau, Wolfbach, Schweina, Querbach, Giehren, Fichtegebirge, and Siegen. In Austria,<sup>10</sup> and Germany there are deposits between Salzburg and Steiermark; in the Tyrols, etc. In Yugoslavia,<sup>11</sup> there are deposits at Aljon, Dob, and Jasikowa. In Norway,<sup>12</sup> there are cobaltiferous fahlbands about Skutterud and Snarum which were once the main producers of the world's cobalt, but they are not rich enough for present-day requirements. Cobaltiferous ore also occurs about Modum. In Sweden,<sup>13</sup> cobaltiferous ore occurs at Gladhammer in Kalmar Län; at Vena near Vettern; at Los in Helsingland; at Tunaberg in Södermannland; and at Hakanbol in Oerebro Län. In Czechoslovakia,<sup>14</sup> there are deposits at Joachimsthal, Bohemia; and at Dobsina, formerly in Hungary. In Italy,<sup>15</sup> cobalt and nickel occur with the copper ores of Switzerland,<sup>16</sup> are cobaltiferous and occur at Valais, Ryr, and Kaltenberg. In Spain,<sup>17</sup> there are cobaltiferous ores in the valley of Gistain, Huesca; and at Guadalcanal, Andalusia. In Portugal,<sup>18</sup> cobalt occurs in the Sierra de Cabreire. In Greece,<sup>19</sup>

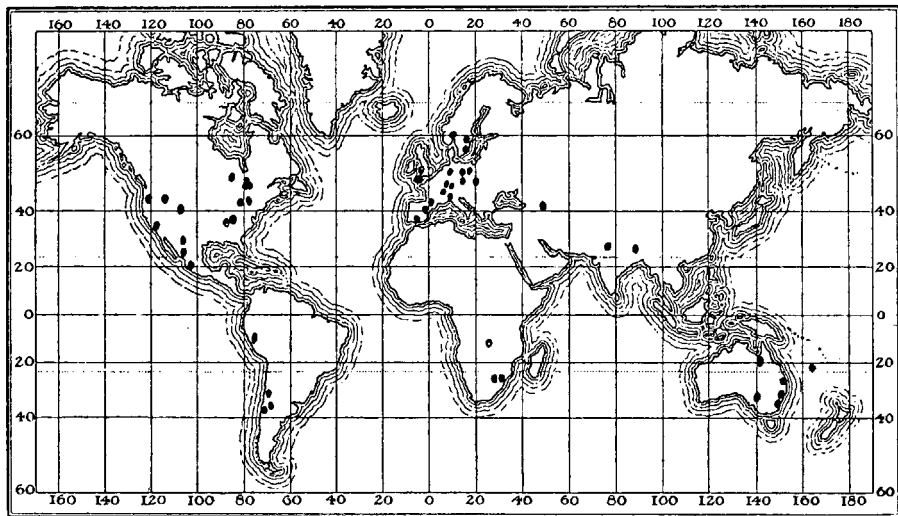


FIG. 1.—The Geographical Distribution of the World's Cobalt Deposits.

only traces of cobalt have been found in the Laurion. In Asiatic Russia,<sup>20</sup> there are abandoned workings at Dachkessan, Government of Elizabetopol, Transcaucasia. In Poland,<sup>21</sup> there are deposits at Miedzianka.

**Asia.** In Persia,<sup>22</sup> cobalt occurs near Täbris, Imam-radsh-David, and Anarak. In India,<sup>23</sup> a mixture of cobaltite and danaite, known as *sehta*, occurs at Khetri and other parts of Rajputana. Small proportions of cobalt occur near Arumanallar, Madras; and Olatura, Kalahandi State. Asbolite occurs at Henzai; erythrite in the Bawdwin mines, Burma; and Linnaite, at Sikkim. In New Caledonia,<sup>24</sup> there are deposits which supplied the major portion of the world's output before the discovery of the Canadian ore. In China,<sup>25</sup> there are deposits near Tsangscheng.

**Africa.** In Algeria,<sup>26</sup> cobalt ores occur near Djebel Tonila. In East Africa,<sup>27</sup> at Kenya. In Belgian Congo,<sup>28</sup> there are cobaltiferous copper ores at Katanga. In the Union of South Africa,<sup>29</sup> several deposits have been located in Transvaal—at Balmoral, Bushveld, Hartbeestfontein, and Wifontein.

**North America.** In Canada,<sup>30</sup> there are the well-known silver-cobalt ores about the cobalt districts, Ontario—e.g., Gowganda, Casey, Otter, Sudbury, Silver Islet; and also near Lake Wendigo, Bay Lake, Gowland Lake, and Lake Superior. There are cobaltiferous minerals east of Big Island Lake, Manitoba. In the United States,<sup>31</sup> there are no large deposits, but there are some cobaltiferous ores near Fredericktown, Missouri; Marion, Kentucky; Grant Co., Prairie City, and Jackson Co., Oregon; Hill Mine, Maryland; Rock-Run, Alabama; Tanana River, Alaska; near Lowell, Massachusetts; Antony's Nose, Pennsylvania; Salina Co., Arkansas; Fort Apache, Arizona; Blackbird, Idaho; Gothic, Colorado; Los Angeles, California; and in the Goodsprings district of Nevada.

In **Mexico**,<sup>32</sup> there are cobaltiferous minerals near Pilhuano, Jalisco; Iturbide, in Chihuahua; Guanacevi and Tamazula, in Durango; Cosala, in Sinalva; and El Boles, in Lower California.

**South America.** In **Argentina**,<sup>33</sup> cobaltiferous ore occurs at Valle Hermosa, province of La Rioja; and in the province of Catamarca. In **Chile**,<sup>34</sup> there are deposits in the province of Atacama, Coquimbo, and Aconcagua. In **Peru**,<sup>35</sup> cobalt occurs in the deposits of Rapi in Ayacucho; and at Vilcabamba in Cuzco. Small occurrences have been reported in **Bolivia**.<sup>36</sup> There are also deposits in Nueva Providencia, **Venezuela**.<sup>37</sup>

**Australasia.** In **New South Wales**,<sup>38</sup> workable deposits occur at Carcoar, Port Macquarie, and Bungonia. There are smaller deposits in several other places. In **Queensland**,<sup>39</sup> cobaltiferous ore occurs near Selwyn; in **South Australia**,<sup>40</sup> at Bimbowrie near Olary; and in **Western Australia**,<sup>41</sup> at Parkerville.

Reliable statistics for the world's output of cobalt are not available. C. W. Drury<sup>42</sup> said that until 1913, the world's annual output of cobalt oxide amounted to about 250 tons, and it then increased, attaining about 400 tons in 1916. Very little, if any, cobalt metal was extracted in 1913, but in 1916, 165 tons of cobalt metal were produced. The approximate outputs of Canada and New Caledonia in tons were:

	1893	1903	1913	1923
New Caledonia . . .	110	414	—	250
Canada . . . . .	—	82	387	396

and according to the Annual Report of the mineral production of Canada for 1928, the outputs, in tons, were:

	1924	1928	1930
Canada . . . . .	423.6	430.0	—
Queensland . . . . .	197.2	7.7	—
Katanga . . . . .	273.2	400.0	—
Chile . . . . .	34.0	—	—
Germany . . . . .	6.0	—	—

According to F. Ullmann, the outputs for cobalt oxide, with 70 per cent. cobalt, cobalt metal, etc., were, in tons:

	1918	1923	1926
Cobalt oxide . . . . .	52.5	20.3	10.0
Cobalt metal . . . . .	21.2	10.2	17.7
Mixed oxides . . . . .	—	—	12.3
Cobalt compounds . . . . .	—	35.4	—

The highest price per lb. for the metal in 1914 was 8s. 4d., and the lowest, 5s. 2½d.; in 1917, the highest price was 8s. 4d., and the lowest, 6s. 3d.; and in 1920, the highest price was 25s., and the lowest 12s. 6d. In 1917, the highest price for the oxide was 6s. 3d., and the lowest 4s. 2d.; and in 1920, the highest price was 17s. 1d., and the lowest, 8s. 2d.

Cobalt almost invariably accompanies nickel, so that analyses of nickel generally show the presence of some cobalt, and *vice versa*—e.g., the analyses of W. R. Barclay,<sup>43</sup> and R. J. McKay. Traces of cobalt have also been observed in numerous nickel ores—e.g., H. Laspeyres found cobalt in *beyrichite*; F. A. Genth, in *millerite*; C. W. Dickson, in *penlandite*; W. F. Hillebrand, and G. Kalb and E. Meyer, in *bravoite*; F. A. Genth, W. F. Hillebrand, and A. Diesseldorf, in *melonite*; C. A. Winkler, in *colloidal nickel silicate*; T. L. Walker, F. Grünling, C. Palmer, and A. Rosati, in *maucherite*; K. Schlossmacher, in *niccolite*; E. Mattiolo, in *breithauptite*; D. Lovisato, in *asite*; F. von Sandberger, in *wolfachite*; H. Laspeyres, in *ballitite*; and A. Brand, in *antimonial nickel*. The analyses of the copper-nickel coinage of Bectria, 146 to 246 B.C., by W. Flight, show the presence of 0.544 per cent. of cobalt. W. Flight also observed cobalt in some old Roman bronzes; and J. Sebelien, in ancient *Egyptian and Mesopotamian bronzes*. A. Cossa in *alum* from Vulcano island; H. D. Richmond and H. Off, in *Egyptian alum*; E. D. Campbell observed cobalt in American pig-irons; J. Pattinson, C. O. Braun, H. Rössler, H. Weiske, F. Wrightson, A. Terreil, G. Lippert, M. Rubach, and O. L. Erdmann, in different kinds of *iron and steel*, and *iron ores*; H. Rössler, in *copper ores* and in

copper ; and F. N. Guild, and C. A. Münster, in *silver ores*—e.g., H. Wurtz, in *huntite* ; D. Forbes, in *arsenical silver* ; I. Domeyko, and A. L. Parsons and E. Thomson, in *proustite* ; H. Wurtz, A. L. Parsons and E. Thomson, and T. L. Walker, in *antimonial silver*, and *discracite* ; and I. Domeyko, in *naumannite*. B. Kosmann reported 0.04 per cent. of cobalt in the *brown iron ore* of Silesia ; F. J. Pope, 0.04 to 0.10 per cent. in the *magnetite* of Ontario ; C. F. Rammelsberg, G. Langhaus, S. P. de Rubies and J. Dorronsoro, L. L. Fermor, and L. G. Eakins, in various samples of *psilomelane* ; L. L. Fermor, J. L. Jarman, S. P. de Rubies and J. Dorronsoro, D. T. Day, W. Gregory, A. Völcker, and H. Rössler, up to 0.7 per cent. in *pyrolusite* ; S. P. de Rubies and J. Dorronsoro, A. Völcker, and W. Gregory, in other *manganese ores* ; J. Murray and A. F. Renard, and J. Y. Buchanan, in deep-sea *manganese nodules* ; G. Natta and M. Strada, in *spinel* ; H. Buttgenbach, in *gummite* ; A. Schöpe, in *renardite*, and in *cornetite* ; W. Campbell and C. W. Knight, C. W. Dickson, R. Beck, A. Stelzner, K. Sauer, C. F. Plattner, H. Schneiderhöhn, C. Bodewig, C. Doelter, H. Laspeyres, F. Kuhlmann, and H. Rössler, in various forms of *pyrites* ; A. Carnot, and A. Beutell, in *arsenical pyrites* ; F. von Sandberger, in *iron glance* ; K. Schulz, and T. Petersen, in *löllingite* ; C. F. Rammelsberg, P. Pilipenko, H. Peltzer, F. von Sandberger, H. A. Hillger, and T. Petersen, in *fahlerz* ; C. Zincken and C. F. Rammelsberg, in *bourbonite* ; A. Carnot, in *bismuth glance* ; C. F. Rammelsberg, in *kobellite*, and in *lillianite* ; F. A. Genth, and T. L. Walker, in *cosalite* ; R. Schneider, in *wittichenite* ; W. Skey, in *köttigite* ; F. Zambonini, in *vesbine* ; S. P. de Rubies, in *chromite*, and in native *platinum* ; F. A. Genth, and G. Frebold, in *zinc blende* ; J. J. Berzelius, F. Stromeyer, H. Rose, and G. Frebold, in *cläusthalite* ; F. Heusler and H. Klinger, and F. Pisani, in *zorgite* ; C. A. Winkler, in *roselite*, and in *rhagite* ; J. J. Berzelius, in *cerite* ; A. Sachs, in *red zinc ore* ; and W. P. Headden, in a Cornish *tin* furnace ; C. A. de Gouvenain, up to 2 per cent.  $\text{Co}_2\text{O}_3$  in the *china-clay* of Allier ; L. Azema, in *clays* from Bordes, in France, and Branchville, in Connecticut ; C. Bischof, in the *clays* of Lower Silesia. G. Bertrand and M. Mokragnatz, W. O. Robinson, J. S. MacHargue, and G. Tissandier discussed the occurrence of cobalt in *soils*. G. Bertrand and M. Mokragnatz found in two samples of arable soils, respectively 0.00028 per cent. of cobalt and 0.00136 per cent. of nickel, and 0.00037 per cent. of cobalt and 0.00174 per cent. of nickel. A. Brongniart observed cobalt in the soils near Paris ; J. Crocq, in the *sands* of Woluwe St. Lambert, near Brussels ; F. Kuhlmann, and W. E. Howarth, in coals ; K. Kraut, in the ashes of various *peats* and *lignites*, and in the *Abraum salts* of the potash works at Eime, Hannover ; A. Stelzner, in the *gneiss* of Himmelsfürst ; H. Rössler, in the *porphyry* of Imsbach ; T. Wherry, in *amethyst* ; and F. von Sandberger, in *hornblende*.

G. Torchhammer,<sup>44</sup> and W. Dittmar observed the presence of traces of cobalt in sea-water ; and S. S. Miholic, in mineral waters. O. Henry, N. P. Hamburg, and M. Mazade detected cobalt in the mineral waters of Nerac, and of Ronneby ; L. de Launay, in the water of Lamalou, Hérault ; F. Jaquot and E. Willm, in the water of Anjou ; R. Nasini and co-workers, in the mineral waters of Roncegno ; C. F. Eichleitner, in those of Orsola ; M. B. Hardin, in the water of Rockbridge Alum Spring, Virginia ; F. W. Clarke, in the water of the Mountain View Mine, Montana ; W. Lindgren, in the water of Cresson Spring, Pennsylvania, and of the Alleghany Springs, Montgomery Co. ; and G. F. Becker, in sinter from the waters of the steam-boat Springs, Nevada.

Cobalt has been noted to occur in traces in some living organisms. G. Forchhammer<sup>45</sup> observed cobalt to occur in marine algæ, and in the ashes of the oak ; T. Wherry, and J. S. MacHargue, in Kentucky blue glass—*Poa pratensis*—and in the soja-bean ; J. Roth, in the ash of the *Zostera marine* ; W. Vernadsky, in different plants ; F. B. Flinn and I. M. Inouye, in a number of plants and sea animals ; and G. Bertrand and M. Mokragnatz discussed the general occurrence of cobalt in various cryptogams and phanerogams. They found minute traces of cobalt in onions, potatoes, spinach, lettuce, cress, tomato, apricots, beans, lentils,

buckwheat, wheat, maize, rice, and mushrooms. The amounts vary from below 0.005 mgrm. to 0.30 mgrm. per kgrm. of the fresh substance. They found both nickel and cobalt in all plants examined, but in very small proportions. The relative proportions of nickel and cobalt present are roughly parallel, organs relatively rich in cobalt being correspondingly rich in nickel. The proportions are highest in the leaves, dried leaves of the following plants named containing the weight indicated (mgrm. per kgrm.) of nickel and cobalt (parenthetical figures): lettuce, 1.51 (0.054); carrot, 1.83 (0.314); spinach, 2.37 (0.74); lime, 2.50 (0.20); apricot, 3.0 (0.40); beech, 3.0 (0.35); cabbage 3.3 (0.07). Seeds or berries, after the leaves, are richest in nickel and cobalt, containing (per kgrm. of dried matter) from 0.14 to 2.25 mgrm. of cobalt in buckwheat and 0.35 mgrm. in lentils, the amount in oats being too small to be determined. The integuments of the berries are richer in nickel and cobalt than the kernels, oat bran containing 0.44 mgrm. of nickel and 0.011 mgrm. of cobalt, and wheat bran 0.39 mgrm. of nickel and 0.011 mgrm. of cobalt. The kernel of decorticated and polished rice is extremely poor in nickel and cobalt, containing only 0.02 and 0.006 mgrm., respectively, this being parallel with the poverty in manganese, zinc, and titanium already noted. Nickel and cobalt are more abundant in the bark than in the wood, beech wood containing 0.12 mgrm. of nickel and 0.01 mgrm. of cobalt and the bark 0.40 and 1.10 mgrm. respectively. The lignified shells protecting certain seeds are poor in both metals. Edible organs or parenchymatous tissues of fruits, roots, bulbs, or tubercles when dry contain moderate amounts of nickel and cobalt, the highest amount found being 3.5 mgrms. of nickel and 2.13 mgrms. of cobalt per kgrm. of dried *cantharellus cibarius*. Nickel and cobalt may act as catalysts in vegetable cells. J. S. McHargue also observed the presence of traces of nickel and cobalt in soils, animals, and plants.

H. M. Fox and H. Ramage observed the presence of cobalt in some animal tissues. The liver of the *Archidoris tuberculata* contained 0.003 per cent. of cobalt, but no nickel. Usually, the cobalt is accompanied by a high proportion of nickel. According to G. Bertrand and M. Machebœuf, cobalt occurs in all the tissues examined, excepting in certain muscles, adipose tissue, and egg-white, in all classes of animals. The organs in general contain rather more cobalt than nickel. The pancreas of all species of animals examined contain relatively large amounts of nickel and cobalt compared with the other organs. P. Dutoit and C. Zbinden also found that cobalt, nickel, and lead accumulates in the pancreas.

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### § 3. The Extraction of Cobalt

The mining of cobalt necessarily varies with the nature of the deposit, and the character of the surrounding rocks. Vein deposits are mined by sinking shafts on or near the veins, and driving from the shafts along the veins. The asbolite ore of New Caledonia is a surface deposit, so that the ore is picked down after the overburden has been removed. The concentration of the ore is partly done by hand-sorting, and partly by wet-gravity, or flotation methods. Neither of these processes is available for the New Caledonia ore, but the hand-picked ore can be concentrated to a matte in a blast-furnace—this was discussed by J. S. Godard,<sup>1</sup> and C. S. Parsons and co-workers.

The metallurgical treatment of the complex cobalt ores involves the recovery of the contained silver, nickel, arsenic, and possibly copper. The primary consideration may be the silver, whilst the other elements are subordinate. Prior to the opening up of the Canadian deposits about 1902, nearly all the world's cobalt was produced in Europe; whilst in Europe the ores were treated for cobalt alone, in Canada, the silver, etc., are recovered. The arsenic, sulphur, copper, iron, and

nickel are associated with the ores of Europe and Canada, but those of New Caledonia contain very little sulphur and arsenic, and relatively a large proportion of manganese. The metal cobalt is not separated from the accompanying metals by dry methods, and wet methods are employed when a separation is needed.

#### A.—Furnace Processes

I. *Arsenical ores*.—In the extraction of cobalt oxide by smelting a mixture of the powdered arsenical ore with limestone and quartz in small blast-furnaces, there are produced (i) a cobalt, nickel, iron, and copper speiss (a regulus of arsenides) or a matte (a regulus of sulphides) containing much silver; (ii) crude silver bullion with about three-fourths of the silver contained in the ore—the remaining silver is contained in the speiss or matte and slag; (iii) a silicate slag which is rejected unless it contains over 10 ozs. of silver per ton; and (iv) a flue-dust of crude arsenious oxide which is re-sublimed and sold. The process of the extraction of the cobalt was described by R. W. Bridges.<sup>2</sup>

The speiss is crushed and ground with 20 per cent. of sodium chloride, and the mixture is roasted in a reverberatory furnace. The chloridized roast is leached with water to remove the excess of sodium chloride as well as soluble compounds of copper, nickel, and cobalt. The copper is precipitated with scrap-iron; and the cobalt and nickel are precipitated as hydrated oxides by means of sodium hydroxide. The precipitate is washed, dried, calcined, and ground. It contains about 40 per cent. cobalt, 3 per cent. nickel, and about 15 ozs. of silver per ton. The residue from the extraction of the chloridized speiss is further extracted with a soln. of sodium thiosulphate to remove silver chloride. The residue is dried, ground, and smelted with quartz to remove most of the iron as slag. The slag still contains silver and cobalt and it is re-worked in the blast-furnace with more ore. The new speiss is treated as before. The final residue is dried; heated with 20 per cent. of sodium nitrite and 10 per cent. of sodium carbonate in a reverberatory furnace. The arsenic is converted into sodium arsenate, which is extracted with hot water. The dried residue has cobalt 30.7 per cent.; nickel, 28.5 per cent.; arsenic, 1.1 per cent.; and silver, 34.6 ozs. per ton; and it is sold to the cobalt and nickel refiners. Modifications of the general method employed by other companies, etc., were described by C. W. Drury, A. A. Cole, J. de Coppet, T. H. Gant, G. M. Dyson, E. Roger, A. J. Wadhams and R. C. Stanley, C. P. Linville, S. B. Wright, F. P. Dewey, C. G. Fink, H. W. Hixon, W. Philipps, J. Savelsberg, R. Sevin, W. Borchers and F. Warlimont, D. Levat, W. Stahl, C. W. B. Natusch, O. Dyckerhoff, P. Manhès, J. Garnier, J. H. Reid, D. Lance, M. Uchino, C. Schreiber, W. Langguth, P. Louyet, O. Barth, C. Guillemain, V. Tafel, F. J. G. Beltzer, H. B. H. Hallowell, W. A. Dixon, and H. Herrenschildt and M. Constable.

At Deloro, Canada, the crushed ore is mixed with the necessary fluxes in a pug-mill and smelted in a blast-furnace for slag, speiss, and crude silver bottoms. The crushed speiss is calcined with a chloridizing roast. The roasted product is extracted with a soln. of sodium cyanide, and the silver precipitated by aluminium dust. The crude silver bottoms from the blast-furnace are heated in an oxidizing atm., whereby the impurities are oxidized and largely eliminated. The silver is further refined by mixing it with the precipitated silver from the cyanide soln., and it is fused with nitre and borax, and cast into bars. The arsenic is recovered as arsenic trioxide in the flues and bag houses connected with the blast-furnace, and when a high degree of purity is desired, it is re-sublimed.

In F. Wöhler's old process for the extraction of cobalt from arsenical ores like smaltite, skutterudite, and cobaltite, 1 part of the powdered ore is fused with 3 parts of potassium carbonate, and 3 parts of sulphur. The cold mass is extracted with water to remove potassium sulphoarsenate; impure cobalt sulphide remains. The treatment with alkali carbonate and sulphur is repeated to remove the arsenic, and there remains cobalt sulphide mixed with the sulphides of nickel, iron, lead, copper, and bismuth. These sulphides are converted into sulphates by treatment

with nitric acid, or by roasting. The acidulated soln. is then treated with hydrogen sulphide to precipitate the sulphides of lead, copper, and bismuth, and the boiling filtrate is treated with nitric acid and calcium carbonate to precipitate a basic salt of iron. The cobalt and nickel sulphates remain in soln. C. G. Richardson roasted the ore with sodium sulphide, or sulphate, or other sulphates—*e.g.*, N. H. M. Dekker used magnesium sulphate,  $4\text{CoAs}_2 + 5(\text{MgSO}_4 \cdot 4\text{H}_2\text{SO}_4) = 4\text{As}_2\text{O}_3 + 4\text{CoSO}_4 + 5\text{MgSO}_4 + 20\text{H}_2\text{O} + 16\text{SO}_2$ . Modifications were described by J. von Liebig, A. Duflos, L. Thompson, L. A. Pélatan, J. W. Neill, H. Herrenschmidt and M. Constable, W. de Witt, N. V. Hybinette, W. Wright, S. F. Hermbstädt, P. Papencordt, O. Dyckerhoff, and H. A. Lewis and F. G. Price. The arsenical ore can also be treated with chlorine fractionally to sublime different chlorides as in the processes of A. L. D. d'Adrian, W. H. Dyson and L. Aitchison, H. T. Kalmus, W. Mc. A. Johnson, and the Metallurgical Development Corporation; W. A. Dixon, and H. A. Megraw heated the arsenical ore to redness in hydrogen chloride to volatilize the arsenic (and zinc) as chlorides, and extracting the mass with water or other solvent. P. M. McKenna tried heating the speiss with boric oxide. J. H. Reid heated the speiss in a vacuum arc-furnace to volatilize fractionally first the sulphur, then the arsenic, then the silver chloride, and finally, at  $3000^\circ$ , the nickel and cobalt. C. G. Fink heated the speiss with calcium carbonate and carbide in an electric vacuum furnace and observed the reaction symbolized:  $2\text{CaO} + \text{CaC}_2 + \text{CoAs}_2 = 2\text{CO} + \text{Ca}_3\text{As}_2 + \text{Co}$ .

II. *Sulphide ores*.—The ore is desulphurized by smelting in a shaft-kiln, and then heating by a blast in a converter, and treating the product as an oxidized ore—*vide infra*. The ore can be heated with silica or silicates, as described by W. Wanjukoff; smelted with polysulphides, or sulphates, carbon and silica, as indicated by R. W. E. McIvor, and J. E. Harding; bessemerized with limestone, as discussed by P. Manhés, N. V. Hybinette, V. Tafel, A. Bremshorst, P. C. Gildchrist and S. G. Thomas, A. Vogt, and J. Savelsberg; or smelted with barium sulphate and silica, as indicated by C. Künzel. P. Manhés used boracite, and B. Bogitsch, sodium sulphate, to facilitate the formation of a slag. There are also processes involving sulphate-roasting, in which sulphates or basic sulphates are found and subsequently leached out with water or dil. acid. They were discussed by W. Borchers and co-workers, O. Barth, R. W. E. McIvor, F. O. Kichline, M. B. Pécourt, Meyer Mineral Separation Co., A. E. Smail, and W. N. Hartley and W. E. B. Blenkinsop. J. A. McLarty oxidized the sulphide ores by heating them in steam under press. E. E. Naef heated the ore mixed with alkali chloride, sulphate, or sulphide, and calcium carbonate, with or without the addition of carbon, in hydrogen and obtained the metal. The Compagnie Electrometallurgique heated the sulphide ore in a resistance furnace between iron electrodes to form iron sulphide and cobalt. P. Manhés heated the sulphide ore with calcium oxide, and chloride or bleaching powder. A. Bremshorst heated the sulphide ore with a mixture of carbon and sodium sulphate, and at  $1300^\circ$  the sulphides of the foreign metals form a mobile liquid which can be poured off the cobalt sulphide. The latter can then be reduced to metal by heating it with carbon. J. Swinburne and E. A. Ashcroft heated the sulphide ore in a converter, treated the product with a molten chloride and chlorine or sulphur monochloride, and then again heated it in a converter, and removed the iron manganese chlorides by volatilization in chlorine. W. McA. Johnson employed a modification of the process.

III. *Oxidized and silicate ores*.—Processes have been devised for treating roasted ores, and oxides, and silicate ores. W. Stahl, and W. Wanjukoff melted the ore with suitable additions to cause the iron to pass into the slag as a silicate or ferrite, and to leave the cobalt and nickel compounds behind. Cobalt is extracted from the copper ores of Katanga by heating them with a little carbon so that only a partial reduction occurs. Most of the copper is reduced to metal, and the cobalt remains with the slag. The slag is then mixed with lime and carbon, and heated

electrically. This produces an alloy of cobalt, copper, iron, and silicon in the respective percentage proportions 30, 26, 40, and 0.7. When a layer rich in cobalt is treated with dil. sulphuric acid, the iron and cobalt pass into soln.—most of the copper remains undissolved. Details were discussed by L. Detrez, and F. Kroll. J. W. Moffat heated the ore with carbon monoxide without fusion, and afterwards melted the metal in an electric furnace. B. Bogitsch heated the ore with carbon and lime. O. Barth melted the ore with carbon, and calcium sulphate. Modifications were described by H. Herrenschmidt and E. Capelle, O. Massenez, W. Mathesius, J. H. Reid, J. Savelsberg, and P. Schwalb. O. Barth heated the oxidized ore in a current of sulphur dioxide and air to convert the cobalt into sulphate and enable it to be leached out with water. Modifications of the process were made by J. G. and C. J. G. Aarts, F. A. Eustis, and W. Savelsberg. C. W. B. Natusch, W. Schöneis, and W. Stahl subjected the oxidized ore to a chloridizing roast and extracted the cobalt chloride with water.

### B.—*Leaching Processes*

S. F. Hermbstädt, and P. Berthier opened the ore by fusion with potassium nitrate; T. Barton and T. B. McGhie, by fusion with sodium carbonate; P. M. McKenna, by fusion of the speiss with boric acid when the heavier nickel speiss separates from the lighter cobalt borate slag; and A. Patera fused a mixture of the roasted ore with calcium, sodium, and potassium nitrates. Some of the cobalt minerals can be opened up by digestion in nitric acid, or in dil. sulphuric or hydrochloric acid mixed with nitric acid. The nitric acid is not needed for earthy cobalt. The roasted ore is more difficult to dissolve than the raw ore. P. Louyet, G. A. Quesneville, A. Patera, B. M. Tassaert, F. Claudet, W. de Witt, and A. Laugier, for example, dissolved the roasted ore in nitric acid; W. McA. Johnson, O. Barth, A. J. Wadhams and R. C. Stanley, F. J. G. Beltzer, A. Drouin, J. de Coppet, H. Lundberg, and A. Carnot, in conc. hydrochloric acid; H. Rosalt, hydrochloric acid and ozonized air; L. J. G. de Burlet, V. N. Hybinette, F. Borchers, O. Barth, C. von Hauer, J. de Coppet, W. Borchers, D. Lance, H. A. Frasch, E. Schulze, M. J. Udy and A. C. Ralston, A. J. Wadhams and R. C. Stanley, and W. Phillips, sulphuric acid; J. B. Readman, sodium sulphate and sulphuric acid; J. von Liebig, and W. Borchers, potassium or sodium hydrosulphate; F. J. C. Beltzer, sodium hydrosulphate and sulphuric acid; F. Gautier, hydrochloric and sulphuric acids; M. Dixon and M. Ratte, sulphurous acid; R. W. E. McIvor, a soln. of magnesium chloride under press.; C. Gabrielli, a soln. of a ferric salt in air; C. W. Drury, a soln. of ferric chloride or sulphate; and H. N. Warren, a hydrochloric acid soln. of copper nitrate. The soln. obtained by extracting the ore with acids can be treated with an excess of ammonia. When the ammoniacal soln. is heated, oxides are precipitated approximately in the order: zinc, cadmium, cobalt, nickel, copper, and silver. Processes based on these reactions were described by H. Caron, C. Gabrielli, D. Lance, M. Malzac, L. Schlecht and co-workers, and V. Varlez.

Speiss, and regulus can be dissolved by making them the anode in an electrolytic cell. In C. C. Cito's method for extracting cobalt and nickel, the ore is treated with copper and fluxes in a reverberatory furnace. An alloy of copper, silver, nickel, cobalt, and arsenic is formed along with a slag. The alloy is cast in anode moulds, and used as anodes in a bath of copper sulphate with sheet-copper cathodes. The copper is deposited on the cathodes, the silver is precipitated as slime, the cobalt and nickel remain in soln., and the arsenic occurs partly in the anode slime, and partly in soln. G. Vortmann based a process on the assumption that if a current be passed through a soln. of nickel and cobalt containing no alkali sulphates or other neutral alkali salts, cobaltous and nickelous hydroxides or basic salts are deposited on the cathode during electrolysis. If the current is reversed, the nickelous hydroxide or basic salt dissolves, whilst cobaltous hydroxide is oxidized to hydrated cobaltic oxide. On repeating the operation a number of times, all the

cobalt can be obtained as hydrated cobaltic oxide, whilst the nickel remains in soln. If a small proportion of a chloride be present in the liquid, the cobaltous hydroxide is converted to cobaltic hydroxide without changing the direction of the current. The separation of cobalt is facilitated by warming. When the precipitation is complete, the current is stopped, and the liquor heated to 60° or 70° whereby a small quantity of nickelous hydroxide remaining with the cobaltic oxide is dissolved. The nickel in soln. is free from cobalt. H. S. Guiterman extracted cobalt by the electrolysis of a soln. of nickel and cobalt chlorides. The chlorine liberated at the anode reacts with the electrolyte to form hydrated cobaltic oxide and free acid. To prevent the electrolyte becoming too acidic, and then dissolving some cobaltic hydroxide, some sodium carbonate is added. Electrolytic processes were also devised by L. J. G. de Burlet, H. H. A. and W. W. Wiggin and A. S. Johnstone, E. E. Armstrong, G. A. le Roy, A. Coehn and E. Salomon, E. Günther, C. L. Mayer, W. Kaiser, L. Münzing, H. A. Frasch, and N. H. M. Del'ker.

In H. Herrenschmidt and M. Constable's process, the powdered wad is made into a thin paste with a soln. of ferrous sulphate, and boiled. Cobalt, nickel, and manganese sulphates pass into soln., whilst iron oxide, silica, and alumina remain as a residue:  $2\text{FeSO}_4 + \text{MnO}_2 \cdot \text{CoO} = \text{Fe}_2\text{O}_3 + \text{MnSO}_4 + \text{CoSO}_4$ ; and  $2\text{FeSO}_4 + \text{Co}_2\text{O}_3 = \text{Fe}_2\text{O}_3 + 2\text{CoSO}_4$ . Sodium sulphide is added to the filtered soln. to precipitate the cobalt, nickel, and manganese as sulphides. A soln. of ferric chloride is now added, and this oxidizes the manganese sulphide to sulphate, which passes into soln.; the cobalt and nickel sulphides are washed, converted into soluble sulphates by roasting, and extracted with water. The sulphates are converted into chlorides by calcium chloride. A fraction of the chloride soln. is treated with milk of lime, and the insoluble cobaltous and nickelous hydroxides which are precipitated are oxidized by chlorine. The washed precipitate is introduced into the remainder of the chlorine soln., stirred, and heated. Black hydrated nickel oxide passes into soln. whilst the cobalt in soln. is precipitated. The result is a soln. of nickel chloride with a suspension of hydrated cobaltic oxide. The latter is separated by filtration, washed, and ignited.

The soln. of cobalt salt associated with salts of other metals has to be treated to isolate the cobalt salt. The process employed depends on the nature of the associated metals, and the solvent. O. Barth said that with sulphuric acid as solvent, lead will be wholly precipitated as sulphate, and that antimony will be precipitated almost completely, and three-fourths of the arsenic as a basic iron salt. Hydrochloric acid soln. will deposit much of the lead as lead chloride, antimony as basic chloride, and antimony and arsenic as basic iron salts.

E. Sack added lead dioxide to a soln. of cobalt, manganese, iron, lead, and aluminium salts and found that all but the cobalt were precipitated. P. Louyet found that iron can be precipitated from a soln. of cobalt and nickel salts, by additions of cobalt hydroxide. T. M. Careis treated a hydrochloric acid soln. of the metals with sodium hydroxide, and dissolved the precipitate in sulphuric acid. The soln. was neutralized with alkali to precipitate copper, iron, and other metals. The cobalt and nickel remaining in soln. were treated with hot ammonium or potassium sulphide to precipitate the nickel. The cobalt was precipitated by zinc as recommended by H. Grosse-Bohle. T. Watanabe described the recovery of 0.05 to 1.0 per cent. of cobalt from cupriferosus pyrites.

Processes for separating salts of foreign metals from the soln. of cobalt salts were suggested by C. H. Aaron, E. F. Anthon, C. F. Bucholz, J. M. Carew, H. Caron, R. S. Carreras, W. A. Dixon, M. Dixon and M. Ratte, J. B. du Faur, H. A. Frasch, J. T. Carrick and B. St. Pattison, C. von Girsowald and co-workers, H. Grothe, J. O. Handy, S. S. Hanes, H. Herrenschmidt, H. Herrenschmidt and E. Capelle, H. Hirtz, C. Hoepfner, W. McA. Johnson, J. P. A. Larson and G. K. L. Helme, A. Laugier, D. M. Liddell, W. Malzac, Metallurgical Development Corporation, Metals Extraction Corporation, Orkla Grube Aktiebolaget, M. B. Pécourt, H. Pederson, G. Perry, the Rhodesia Broken Hill Development Co., H. Rosalt, E. Sack, C. F. Schantz, G. Schreiber, La Société Anonyme des Établissements Malétra, S. P. L. Sörenson, E. A. Sperry, W. Stahl, A. Taraud and



co-workers, J. H. Thwaites, J. H. Thwaites and S. J. Ralph, M. J. Udy and O. C. Ralston, A. J. Wadhams and R. C. Stanley, H. N. Warren, A. Weissenborn, H. H. A. and W. W. Wiggan and A. S. Johnstone, C. Winkelblech, and G. C. Wittstein.

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#### § 4. The Separation of Cobalt and Nickel

Many processes have been proposed for the separation of cobalt and nickel for analytical purposes, and for preparing nickel and cobalt of a high degree of purity. Only a few are suited to give good, clean separations. Some are rough separations where extreme purification is not usually so important. The subject was discussed by R. Fischer,<sup>1</sup> F. Gauhe, and C. Krauss.

(i) A. Laugier digested the mixed precipitate of cobalt, nickel and iron hydroxides with an excess of a soln. of oxalic acid, and removed the soluble iron oxalate by filtration and washing. The insoluble oxalates were dissolved in ammonia, and on exposing the filtered soln. to air for several days ammonium nickel oxalate and manganese oxalate were deposited, whilst cobalt oxalate above remained in soln. F. Stromeyer, P. Louyet, E. F. Anthon, W. de Witt, C. Winkelblech, C. Künzel, and G. A. Quesneville used modifications of this process. A. Carnot said that when a soln. containing alkali or ammonium oxalate, is treated with

ammonium sulphide, nickel remains in soln. as a sulpho-salt, but the cobalt is precipitated as sulphide.

(ii) According to R. Phillips, and G. C. Wittstein, if a soln. of the two oxides in an excess of acid is supersaturated with ammonia, diluted with air-free water, and treated with potassium hydroxide, nickel oxide is first precipitated, and the cobalt remains in the filtrate. J. J. Berzelius added that, if air-free water is not employed or if the liquor after treatment with potash-lye is exposed to air, cobaltic oxide is precipitated along with the nickel oxide.

(iii) J. Persoz separated the two oxides by dissolving them in hydrochloric or nitric acid, saturating the soln. with phosphoric acid, adding ammonia until the precipitate first produced is re-dissolved, and exposing the soln. to air. The phosphate precipitation process in the presence of acetic acid was examined by M. S. Cheney and E. S. Richards, J. Hope, J. Persoz, T. H. Henry, G. Schreiber, G. Perry, S. P. L. Sørensen, P. Dirvell, and H. Baubigny.

(iv) T. Barton and T. B. McGhie proposed separating the two chlorides by the fractional crystallization of the slightly acidified chloride soln.; R. S. Carreras, by the fractional crystallization of the sulphates; and J. H. Reid, by the fractional precipitation of the orthophosphate.

(v) J. B. Richter separated the two salts by crystallization from a soln. containing a large quantity of ammonium sulphate.

(vi) C. F. Bucholz, and D. Lance proposed separating cobalt and nickel oxides by fractional precipitation with ammonia, or by dissolving the oxides in ammonia after precipitation. F. Pisani also described a modification of the process.

(vii) J. L. Proust treated a soln. of the two oxides in sulphuric acid with potassium hydroxide, and found that the less soluble potassium nickel sulphate separates out first, but several repetitions of the process are necessary.

(viii) J. von Liebig found that potassium nickel cyanide is decomposed by acids under conditions where the corresponding cobalt salt is not decomposed. Hence, potassium cyanide is added to an acidulated soln. of the two metals until the precipitate re-dissolves. The soln. is gently heated, and after cooling, it is treated with dil. sulphuric acid and filtered. The filtrate is treated with nitre, evaporated, and ignited for cobaltic oxide. The precipitate is decomposed by potassium hydroxide or carbonate into soluble potassium cobalt cyanide, and insoluble nickel hydroxide or carbonate. J. von Liebig, and T. H. Henry found that this process is not quite satisfactory because the nickel always contains some cobalt.

J. von Liebig obtained satisfactory results by modifying the process. The mixed oxides are treated first with hydrocyanic acid, and then with potash-lye, and the liquid is warmed till all is dissolved. The soln. is boiled to expel hydrocyanic acid, and the potassium cobaltous cyanide is converted into potassium cobaltic cyanide by chlorine or bromine, whilst the nickel remains in soln. as a complex cyanide. Finely-powdered mercuric oxide is added to the warm soln. to precipitate the nickel partly as oxide and partly as cyanide. The ignition of the washed precipitate furnishes nickel free from cobalt. The filtrate is supersaturated with acetic acid, and the boiling soln. is treated with cupric sulphate, whereby copper cobalt cyanide is precipitated. The precipitate becomes granular if the mixture is boiled for some time. It is then filtered, washed, and dissolved in hydrochloric acid. The soln. is treated with a little nitric acid, then with hydrogen sulphide. The filtrate is boiled for a moment to expel the hydrogen sulphide, treated with boiling potassium hydroxide, and the precipitated cobalt hydroxide is well washed, dried, and ignited for cobaltic oxide free from nickel.

The process was discussed by A. Carnot, E. Fleischer, O. W. Gibbs, F. Wöhler, F. Gauhe, A. Guyard and H. Tamm, J. F. Hambly, A. Jorissen, H. Kämmerer, A. Kläye and A. Deus, L. L. de Koninck, C. H. John, W. E. Pawlow, J. S. C. Wells and H. T. Vulté, and C. Zimmermann. H. Fleck, and A. Guyard observed that when the ammonium sulphide precipitate is treated with a soln. of potassium cyanide, only the nickel passes into soln. J. A. Sanchez found that the cobalt is precipitated from a cyanide soln. by silver nitrate, the nickel remains in soln.

(ix) H. Rose treated a hydrochloric acid soln. of the mixed oxides with chlorine

to form cobaltic chloride. The soln. is then treated with an excess of barium carbonate and allowed to stand in the cold for about 18 hrs. with frequent agitation. The precipitated cobaltic oxide mixed with the excess of barium carbonate is dissolved in hot hydrochloric acid. The barium is removed as sulphate, and the cobalt precipitated by potassium hydroxide. The filtrate containing nickel and barium chlorides is similarly treated to remove the barium as sulphate, and then the nickel as hydroxide. The process was examined by J. D. Smith, T. H. Henry, T. Fleitmann, E. Donath, T. Moore, and R. L. Taylor.

(x) F. Claudet added ammonium chloride to a nitric acid soln. of the mixed oxides, saturated the liquor with ammonia, and agitated it with air or oxygen and boiled with an excess of hydrochloric acid, whereby cobalt purpureochloride,  $[\text{CoCl}(\text{NH}_3)_5]\text{Cl}_2$ , is precipitated. The method was recommended by S. P. L. Sørensen, and H. Copaux as a useful process for preparing pure cobalt; and T. W. Richards and G. P. Baxter employed the process for purifying cobalt for their at. wt. determinations. Modifications were described by R. Phillips, W. de Witt, H. A. Frasch, G. T. Morgan and J. D. M. Smith, G. Schuster, H. Grothe, and H. Rose. S. P. L. Sørensen's directions are :

The carbonate—say 20 grms.—is dissolved in the smallest quantity of hydrochloric acid (1 : 1); and to the filtered and cooled soln. is added a mixture of 250 c.c. of conc. aq. ammonia, and 50 grms. of ammonium carbonate dissolved in 250 c.c. of water. A current of air is passed through the liquid for 3 hrs. The soln. is now mixed with 150 grms. of ammonium chloride, and evaporated on a water-bath for a couple of hours, when a mush is produced. This is stirred up with dil. hydrochloric acid. If any carbon dioxide is developed, the liquid is slightly over-saturated with ammonia by adding 10 c.c. of the conc. aq. soln. The 400 to 500 c.c. of liquid are heated for an hour on the water-bath : 300 c.c. of conc. hydrochloric acid are added, and all is warmed on a water-bath for half to three-quarters of an hour. The ammine salt is then filtered from the cold liquid; washed with hydrochloric acid (1 : 1) until freed from ammonium chloride; and then washed with alcohol until freed from acid. The yield is 3.45 grms. The salt can be re-crystallized by dissolution in about 400 c.c. of 2 per cent. aq. ammonia, filtered, and then mixed with 300 c.c. of conc. hydrochloric acid, etc., as before. The yield is now 33 grms. The salt can be reduced to cobalt by heating it in a stream of hydrogen; it can be converted into oxide by fusion with sodium carbonate, or by heating it with nitric acid, evaporating the soln. to dryness, and heating the product until nitrogen oxides are no longer evolved.

(xi) A process has been devised which is based on the reaction discovered by N. W. Fischer, that when potassium nitrite is added to an acetic acid soln. of a cobalt salt, potassium nitritocobaltate is precipitated, whilst nickel does not yield an insoluble salt under these conditions. Observations on this subject were made by A. Stromeyer, W. de Witt, V. Dreyer and A. Richter, H. Pützer, H. Nitze, O. W. Gibbs and F. A. Genth, A. Duflos and N. W. Fischer, O. Brunck, E. Murmann, O. Köttig, B. Brauner, H. Rose, O. L. Erdmann, F. Gauhe, A. Streng, H. Baubigny, J. B. Mackintosh, T. Fleitmann, S. R. Benedict, H. Bötticher, and H. Copaux. T. W. Richards and G. P. Baxter employed the process in purifying cobalt for their at. wt. determinations.

(xii) According to M. Ilinsky and G. von Knorre, if a soln. of nitroso- $\beta$ -naphthol be added to a mixed soln. of cobalt and nickel salts, a bulky precipitate of the cobalt salt is produced, whereas nickel gives no such precipitate. The process is used for separating small amounts of cobalt from large amounts of nickel; it was examined by R. Fischer, H. Copaux, C. Krauss, L. L. de Koninck, R. Burgess, A. Eder, P. Ślawik, K. Wagenmann, L. A. Congdon and T. H. Chen, F. G. Germuth, W. H. Chapin, and C. Meineke.

(xiii) O. Brunck observed that if an excess of  $\alpha$ -dimethylglyoxime be added to a strongly ammoniacal soln. of cobalt and nickel salts, the nickel salt alone gave a precipitate of the complex salt. The process is useful for separating a small proportion of nickel from a large proportion of cobalt; it was examined by L. Tschugaeff, K. Kraut, A. Ivanicky, H. Wdowiszewsky, F. Feigl and H. J. Kapulitzas, F. G. Germuth, V. Cuvelier, A. R. Middleton and H. L. Miller,

P. Bogoluboff, L. V. W. Spring, F. Ibbotson, H. Pederson, and S. W. Parr and J. M. Lindgren.

(xiv) H. Grossmann and co-workers found that dicyanodiamidine sulphate likewise precipitates relatively small proportions of nickel from large proportions of cobalt.

(xv) R. Fischer, and A. Carnot obtained an imperfect separation of cobaltic oxide by adding hydrogen dioxide to the cold soln. of nickel and cobalt salts either before or after saturation with ammonia. The separation is not complete. A. Carnot found that if hydrogen dioxide, ammonium chloride, and ammonia is added to a mixed soln. of cobalt and nickel salts, and the soln. is treated with ammonium molybdate and an excess of acetic acid, a bulky, rose-coloured precipitate of cobalt molybdate is formed, which, when heated to redness, has the composition  $2\text{CoO} \cdot 7\text{MoO}_3$ .

(xvi) E. Sack, J. D. Smith, and W. J. Harshaw treated the soln. of sulphate with the calculated quantity of lead dioxide when hydrated cobalt oxide is precipitated, and nickel sulphate remains in soln.

(xvii) A. Coehn and E. Salomon found that hydrated cobalt oxide is precipitated by the addition of a persulphate, say ammonium persulphate, to the soln., and nickel salt remains in soln.

(xviii) According to P. Louyet, and A. Patera, if bleaching powder is added to a mixed soln. of the salts, manganese peroxide is first precipitated, then cobaltic oxide, and lastly nickel. The process, using as oxidizing agents, sodium or calcium hypochlorite, sodium hypobromite, potassium hydroxide and bromine, or sodium hypochlorite and ammonia, was applied by T. Fleitmann, E. Donath, A. Carnot, J. Bernard, T. H. Gant, C. von Hauer, G. Schreiber, A. von Kripp, W. McA. Johnson, G. Selve, O. Barth, F. H. Rhodes and H. J. Hosking, M. J. Udy and O. C. Ralston, E. J. Mills and J. J. Smith, O. W. Gibbs, G. Delvaux, R. L. Taylor, H. Rose, O. Popp, T. H. Henry, O. C. Ralston, C. W. Drury, H. N. Warren, K. S. Guiterman, P. Berthier, G. Vortmann, A. Terreil, C. Krauss, and A. Jorissen. Modifications in which, say, chlorine is passed into alkali-lye in the presence of the mixed hydrated oxides, were described by W. A. Dixon, H. Herrenschildt, and La Société Anonyme des Établissements Malétra.

In applying the process, the mixed oxide is dissolved in hydrochloric acid. Powdered calcium carbonate is added to the warm liquor gradually, with stirring, until no further precipitate is obtained. The precipitate of iron, arsenic, and silica is removed by filtration, and the soln. is treated with bleaching powder added slowly, with stirring, until nearly all the cobalt is precipitated as black oxide. Very little nickel is precipitated. The washed and dried precipitate is calcined for cobalt oxide. The oxide is boiled with a soln. of sodium carbonate to convert calcium sulphate to carbonate. The precipitate is washed with dil. hydrochloric acid, then with water, and finally dried and calcined. According to H. T. Kalmus, the initial and final products of this treatment had the composition :

	Co	Ni	Fe	S	As	SiO <sub>2</sub>	Ca
Crude oxide . . .	70.36	1.12	0.82	0.45	0.10	0.20	0.50
Purified oxide . . .	71.99	0.041	0.11	0.02	none	none	0.02

(xix) A. Rosenheim and E. Huldshinsky treated the soln. of mixed salts with an excess of ammonium thiocyanate, and extracted the cobalt salt by a mixture of amyl alcohol and ether (1 : 25). The nickel salt remains in the aq. layer. The process was discussed by W. Skey, C. H. Wolf, H. W. Vogel, M. Pritze, A. D. Powell, and H. Grossmann.

(xx) E. Pinerua, J. Renner, and F. S. Havens found that whilst cobalt chloride is readily soluble in ether saturated with hydrogen chloride, nickel chloride when similarly treated gives a yellow precipitate.

(xxi) L. Mond based a process for the separation of nickel on the fact that nickel readily combines with carbon monoxide at 50° to 80° to form a volatile carbonyl which decomposes at a higher temp., whilst cobalt under similar conditions does not form a carbonyl. The process was discussed by W. Singleton, and W. C. Roberts-Austen.

(xxii) H. Delffs found that if insufficient sodium acetate for complete decomposition be added to a soln. of cobalt and nickel nitrates, and the liquid treated with hydrogen sulphide, cobalt is precipitated free from nickel, or nickel free from cobalt, according to the proportion of sodium acetate employed.

(xxiii) J. H. Vivian thought that it would be possible to separate cobalt and nickel by taking advantage of the different affinities of the two elements for arsenic.

(xxiv) T. L. Phipson, L. Compin, W. Singleton, E. Cattelain, A. Whitby and J. P. Beardwood, and E. D. Campbell found that potassium xanthate precipitates both cobalt and nickel xanthates; when a few drops of ammonia are added, the nickel passes into soln. whilst the cobalt xanthate can be collected on filter-paper.

(xxv) W. R. Omdorff and M. L. Nichols found that cobalt in neutral soln. is precipitated by dinitrosoresorcin, and that it can be thus separated from a small proportion of nickel.

(xxvi) A. Carnot proposed separating small proportions of nickel from cobalt by adding ammonium molybdate to a soln. containing an excess of ammonium chloride, ammonia, and hydrogen dioxide. Cobalt molybdate is precipitated. L. A. Congdon and T. H. Chen did not obtain good results, owing to the difficulty of adding the exact amount of ammonium molybdate required for the purpose.

(xxvii) The fractional precipitation of cobalt as ammonium cobalt phosphate and weighing as cobalt pyrophosphate has been discussed by J. Clark, L. A. Congdon and T. H. Chen, H. D. Dakin, J. Dick, P. Dirvell, J. Hope, R. Strebing and J. Pollak, C. S. Tatlock, and H. H. Willard and D. Hall.

(xxviii) P. Gucci evaporated a soln. of the two metals to dryness, heated the residue in molten potassium nitrate, extracted the mass with hot water, and extracted the nickel from the residue by dil. nitric acid. C. Krauss said that the separation is incomplete.

(xxix) E. A. Demarçay observed that when an ammoniacal soln. is treated with zinc, the nickel is precipitated before the cobalt.

(xxx) L. Thompson treated with ammonium carbonate a soln. containing ammonium chloride and found that the nickel remains in soln. and the cobalt is precipitated. C. Winkler said that the separation is qualitative and not quantitative.

(xxxi) K. Flick based a process on the fractional decomposition of the sulphates by heat.

J. V. Dubsky and V. Dostal studied the purification of cobalt salts from nickel through the formation of complex amines. Methods for the separation of cobalt and nickel electrolytically in analytical work, etc., have been proposed by E. Basse and G. Selve,<sup>2</sup> W. J. Harshaw, R. L. Suhl and co-workers, W. D. Bancroft, C. A. Kohn and J. Woodgate, J. E. Root, G. Vortmann, A. Coehn and E. Salomon, A. Coehn and M. Gläser, A. Classen, D. Balachowsky, E. F. Smith, S. A. Pleteneff and W. W. Kusnezowa, and H. H. Alvarez. In the opinion of B. Neumann, F. M. Perkin, E. F. Smith, O. P. Watts, and P. Bruylants, the proposed methods are not satisfactory. P. Röntgen and R. Buchkremer discussed the effect of cobalt in zinc electrolytes in reducing the yield.

There are some monographs and textbooks dealing with the metallurgy of cobalt. For instance:

L. Ouvrard, *Industries du Chrom, du manganese, du nickel, et du cobalt*, Paris, 1910; E. Prost, *Cours de métallurgie des métaux autres que le fer*, Paris, 1912; C. Schnabel, *Handbuch der Metallhüttenkunde*, Berlin, 1904; London, 2. 753, 1907; C. W. Drury, *Cobalt—its Occurrence, Metallurgy, Uses and Alloys*, Toronto, 1919; H. Herrenschmidt and E. Capelle, *Le cobalt et le nickel*, Rouen, 1885; M. Fourment and L. Guillet, *Métallurgies du plomb du nickel et du cobalt et alliages de ces métaux*, Paris, 1926; H. Copaux, *Recherches expérimentales sur le cobalt et le nickel*, Paris, 1905; J. Meunier, *Cobalt et nickel*, Paris, 1889; A. M. Villon, *ib.*, Paris, 1891; V. Tafel, *Lehrbuch du Metallhüttenkunde*, Leipzig, 2. 523, 1929; A. Weissenborn, *Metallbörse*, 17. 1716, 1826, 1927; D. M. Liddell, *Handbuch of Non-ferrous Metallurgy*, New York, 2. 1279, 1926.

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## § 5. The Preparation of Metallic Cobalt

Cobalt is fairly readily reduced from its compounds. According to E. D. Clarke,<sup>1</sup> cobalt oxide is reduced to the metal in the oxyhydrogen flame. F. O. C. Gren, W. A. Lampadius, W. Hankel, B. M. Tassaert, P. Berthier, G. Selve and F. Lotter,

H. T. Kalmus, and H. Moissan found that the oxide is reduced by heating it in a carbon crucible, or by heating it when admixed with carbon or starch. C. Winkler heated a mixture of cobaltous oxide and 10 to 12 per cent. of starch or wheat meal, covered with pieces of charcoal, in a porcelain crucible at a white-heat for an hour. There is formed a spongy metal which can easily be crushed to powder; if the heat be too intense, the metal appears in thick plates. To remove carbon from the metal, the product can be mixed with 25 to 30 per cent. of cobalt oxide, and melted. L. Thompson reduced the oxide by potassium tartrate in a carbon crucible, and the product containing about 4 per cent. of carbon was then melted with cobalt oxide and borax in a crucible lined with alumina. H. Moissan, and D. M. Liddell reduced the metal in an electric furnace. H. T. Kalmus said that the reduction of cobalt oxide by anthracite required 1 hour at 1200° for complete reduction under conditions where with charcoal, or lampblack, the reduction is completed in 1 hour at 900°, and in 10 minutes at 1000° to 1100°. About 20–30 per cent. more carbon was employed than corresponds with the equation:  $2\text{Co}_3\text{O}_4 + 4\text{C} = 6\text{Co} + 4\text{CO}_2$ . The application to industrial processes was discussed by A. L. D. d'Adrian, L. P. Basset, and S. B. Wright. B. Bogitch investigated the reduction of cobalt oxide by carbon monoxide, wood-charcoal, and coal. If the temp. is high enough for the slag to separate, the degree of reduction is independent of the proportion of reducing agent present. The rapid fusion of the oxide ore prevents a state of equilibrium between the ore and the reducing agent being established. C. G. Fink used calcium carbide as reducing agent. J. J. Berzelius, J. W. Döbereiner, H. St. C. Deville, and R. Schneider reduced cobalt oxalate to metal by heating it to redness; and, according to H. Moissan, cobalt oxide begins to be reduced by carbon monoxide at about 300°; and H. T. Kalmus found that between 500° and 750°, over 90 per cent. of cobaltous oxide is reduced by carbon monoxide in a few minutes, but the remainder is reduced very slowly at that temp.; between 750° and 900°, the part that is not reduced in the first few minutes is smaller the higher is the temp. At 900°, about 98.8 per cent. is reduced in the first few minutes. At low temp., say between 350° and 450°, the finely-divided metal acts on the carbon monoxide with the separation of carbon. The subject was studied by B. Bogitch, L. Mond and co-workers, the Farbenindustrie Aktien Gesellschaft, and the Badische Anilin- und Sodafabrik. J. Jahn, and V. Tafel observed that, unlike nickel oxide, cobalt oxide is reduced by water-gas at 250° to 350°. H. T. Kalmus said that producer gas is the cheapest reducing agent to employ for industrial purposes, and that the metallic product should be cooled in a reducing atmosphere. P. E. Martin, and D. Mendeléeff reduced the oxide by heating it in a current of hydrocarbons.

C Brunner reduced ammonium cobalt oxalate to metal by heating it in a closed crucible. H. Copaux observed that the product of the action of heat on cobalt oxalate is a mixture of cobalt, and cobalt oxide, and that the reduction should be completed by heating the product in hydrogen. W. Biltz said that a very reactive form of cobalt is obtained rapidly by heating to redness in hydrogen, at 120°; the powdered and dried oxalate. The product is powdered and again heated in hydrogen. A. Brochet observed that the cobalt obtained from the oxalate is not pyrophoric. W. O. Snelling obtained the metal by heating the formate at a low temp. in vacuo, or in hydrogen. The metal is very reactive, but, according to A. Brochet, it is not pyrophoric. J. Riban observed that some metal, as well as oxide, is formed when a soln. of cobalt formate is heated at 175° in a sealed and evacuated vessel.

W. Müller, C. H. Wolff, A. Sieverts, G. Magnus, C. Zimmermann, J. Jahn, and W. Ohl observed that the oxide or oxalate is reduced by heating it in a current of hydrogen. W. Müller, F. Glaser, and G. Gallo thought that a suboxide is formed—*vide infra*. W. Müller said that the reduction of cobalt oxide by hydrogen begins at 320°; H. Moissan, 190° to 200°, and that pyrophoric metal can be formed at 250°; and F. Glaser observed that the reduction of the oxide occurs at 228°, and that the

weights obtained at 250°, 306°, and 298° are constant, owing to the intermediate formation of hydrides. T. W. Richards and G. P. Baxter observed that cobalt oxide is only slowly reduced by hydrogen at the temp. available in a hard glass tube. G. Gallo said that 'he reduction begins at 118°, and is completed in 4 hrs. at 400°, in 15 minutes at 700°. G. F. Hüttig and R. Kassler observed the yield obtained by heating hydrated cobaltic oxide in hydrogen for 5 hrs. at :

	250°	300°	350°	400°	500°
Cobalt.	77.52	84.25	91.82	99.34	99.86 per cent.

H. T. Kalmus obtained a 90 per cent. reduction in a few minutes between 500° and 700°, but the subsequent progress of the reaction was slow ; and as the temp. rises from 700° to 1100°, the proportion reduced in the first few minutes with rise of temp. rapidly increases to 100 per cent. Thus :

	609°				824°			1073°			
Time	7	15	30	60	2.5	30	150	1	5	30	60 mins.
Reduction	62.2	81.8	83.0	93.0	98.5	99.0	99.2	90.0	99.4	99.8	100 per cent.

when the product is cooled in hydrogen. The reduction of the oxide for industrial purposes was described by T. A. Edison, and H. C. Hubbell ; and for the preparation of a cobalt catalyst, by the Farbenindustrie Aktien Gesellschaft, I. L. Fohlin, C. Ellis ; and H. S. Taylor and R. M. Burns, E. Péligot, and W. Spring obtained crystals of cobalt by reducing the cobalt chloride in hydrogen ; and C. Winkler, and W. Spring obtained mirrors of cobalt by reducing the vapour of the chloride with hydrogen.

H. Rose obtained cobalt by heating a mixture of cobalt oxide and ammonium chloride. T. W. Richards and G. P. Baxter said that a spongy metal is produced when the oxide is reduced by heating it in a current of ammonia ; C. Winkler said that the metal appears as a black powder which glows in air. C. Winkler, and B. Kerl reduced cobalt chloride by heating it in ammonia. E. Péligot, E. H. von Baumhauer, R. Schneider, W. Sharwood, W. Casselmann, S. P. L. Sørensen, and F. Claudet obtained cobalt by heating the chloride or the aminochloride in hydrogen.

J. Jahn, and H. T. Kalmus reduced the oxide by aluminium in the thermite process. The thermal value of the reaction is :  $3\text{Co}_3\text{O}_4 + 8\text{Al} = 4\text{Al}_2\text{O}_3 + 9\text{Co} + 9.902 \text{ Cals.}$  L. Weiss and O. Aichel used mischmetal instead of aluminium. H. Moissan obtained cobalt by the distillation of the amalgam.

H. St. C. Deville melted cobalt in a lime crucible standing inside a graphite crucible ; A. A. Valenciennes employed a magnesia crucible arranged in a similar way. C. Winkler melted the cobalt along with about 25 per cent. of cobalt oxide in a porcelain crucible. The Berndorfer Metallwarenfabrik reduced the oxide to metal, moistened the metal with a 4 per cent. soln. of potassium permanganate, and melted the product in a suitable furnace. H. Copaux said that cobalt takes up silica from the so-called magnesia or alumina crucibles, and he recommended crucibles made of aluminium silicate bonded with calcium aluminate.

A. C. and E. Becquerel obtained a bright deposit of cobalt by the electrolysis of a soln. of cobalt chloride which had been neutralized with ammonia or potassium hydroxide. A. Gaiffe, H. T. Kalmus, L. Schlucht, H. Fresenius and F. Bergmann, and F. Mylius and O. Fromm used a similar process. C. Winkler recommended 100 c.c. of a soln. of cobalt sulphate having 11.62 grms. of cobalt per litre, 30 grms. of aq. ammonia of sp. gr. 0.905, and 500 c.c. of water. The electrodes consisted of two platinum plates, 9.4 cms.  $\times$  5.9 cms. ; and the current employed was 0.7 amp. at 3 volts.

A. C. Becquerel observed that *copper* immersed in a soln. of sodium cobalt chloride, acquires a coating of cobalt. According to Z. Roussin, D. Vitali, A. Siemens, and A. Commaille, *magnesium* deposits cobalt from slightly acid soln. of

cobaltous salts. S. Kern obtained an incomplete precipitation as hydrated oxide ; and K. Seubert and A. Schmidt obtained a complete precipitation as cobaltous hydroxide. T. M. Careis, H. Grosse-Bohle, The Farbenindustrie Aktien Gesellschaft, A. E. Demarçay, Z. Roussin, and J. L. Davies reduced cobalt from soln. of cobalt salts by means of *zinc*. N. W. Fischer obtained no precipitation with soln. of cobalt nitrate. According to L. de Boisbaudran, cobalt is not precipitated from neutral soln. by zinc except in the presence of a metal easily reducible by zinc—e.g., lead or copper, but not cadmium ; if a copper salt be present, copper alone is deposited if the liquid is acidic. F. Stolba, and C. Mène obtained analogous results with zinc, and L. de Boisbaudran, with *cadmium*. R. Kremann and co-workers observed that with a soln. of cobalt sulphate at ordinary temp., zinc or cadmium precipitates cobalt largely in a form of cobaltous hydroxide ; but less hydroxide is formed at 100°. The reaction is not only dependent on the temp. but also on the ratio, Co : Zn, or Co : Cd, and on the conc. of the soln. The cobalt forms a solid film or an alloy at the surface of the precipitant. M. Centnerszwer and J. Drucker studied the effect of the conc. of the soln. on the reaction. R. Müller and F. R. Thois observed an incomplete precipitation by zinc or cadmium with a soln. of cobaltous chloride in ethyl alcohol. A. Damour obtained cobalt amalgam by the action of zinc amalgam on a soln. of a cobalt salt. C. Formenti and M. Levi observed that *aluminium* precipitates cobalt as a black powder from soln. of the nitrate, acetate, or chloride. W. C. Reid found that *thallium* deposits a basic salt from a soln. of cobalt nitrate. O. Prelinger found *manganese* precipitates cobalt from soln. of cobalt salts ; and M. Perry, that *iron* precipitates cobalt first from a mixed soln. of salts of cobalt, iron, nickel, and manganese. L. Kritschewsky observed that *hydrogenized palladium* does not reduce a soln. of a cobalt salt to metal ; and B. Neumann, that hydrogen in the presence of palladium does not precipitate cobalt from a soln. of its simple or complex salts. W. Ipatéeff and B. Zragin found that under a press. of 100 atm. *hydrogen* precipitates a mixture of cobalt and cobalt sulphate from 2*N*-CoSO<sub>4</sub> and 0.2*N*-CoSO<sub>4</sub>, but with 4 days' heating, the reaction is not completed ; at 100°, soln. of the nitrate give no metal ; but with chloride soln., there is a small yield of metal. J. H. Weibel said that the separation of cobalt and cobalt oxide by hydrogen or carbon monoxide begins at 250° ; but at 300°, only cobalt is formed. The subject was further examined by the Farbenindustrie Aktien Gesellschaft, and W. D. Richardson. T. W. Richards and G. P. Baxter<sup>2</sup> found that an ammoniacal nitrate soln. furnishes an oxy-salt which makes the electrolysis impossible ; but an ammoniacal soln. of the sulphate furnishes a good deposit with a current density of 0.7 amp. per sq. dm. E. Vogel obtained spongy deposits with 0.5*N*-CoSO<sub>4</sub> and 0.1*N*-CoSO<sub>4</sub> and 8.5 amps. per sq. dm. According to H. G. Denham and S. W. Penny-cuick, reproducible cobalt electrodes are formed by deposition on platinum from a soln. of cobalt chloride containing 2 c.c. of a 5 per cent. soln. of phosphoric acid, 20 c.c. of a 10 per cent. soln. of sodium dihydrophosphate, and 2 c.c. of a sat. soln. of sodium dihydrophosphite and a current density of 0.008 amp. per sq. dm. during 24 hrs.

B. Neumann observed that the deposits obtained from a soln. of cobalt chloride or sulphate and boric acid are hard, bright, and white, but readily peel off if too thick. G. B. Bomino and M. Bottini obtained *cobaltized cobalt*—analogous to platinized platinum—on platinum from a soln. of cobalt and ammonium sulphates, using 4.5 volts for half an hour, and then 50 to 60 volts for 1 minute. E. Müller and P. Spitzer obtained a deposit of spongy cobalt on platinum with a very high current density, and an acidified soln. of cobalt sulphate. A. Estelle produced cobalt as a fine powder by the electrolysis of a neutral soln. of a cobalt salt mixed with an organic hydroxyl-compound like sugar or glycerol. According to V. Kohlschütter and F. Jakober, the contraction developed by the deposition of a film of cobalt on platinum depends on the current density, temp., and composition of the electrolyte.

F. Mylius and O. Fromm found that with a cobalt cathode on the bottom of

a sat. soln. of cobalt sulphate, and a platinum wire anode, flecks of cobalt appear on the surface of the soln.

R. Schildbach observed that the occluded hydrogen is greater at low temp., and is very small at higher temp., and this hydrogen causes a fall of potential after the current is broken. With a neutral soln. of cobalt sulphate at 0°, 20°, 50°, and 92°, the fall of potential was, respectively, 45, 18, 9, and 4 millivolts. Observations were made by F. Förster, H. T. Kalmus, M. M. Raessler, O. P. Watts, C. Winkler, and R. Schildbach discussed the presence of oxide in electro-deposited cobalt. A. C. and E. Becquerel, and M. M. Raessler noted the contamination of the deposit with iron.

According to G. Coffetti and F. Förster, some hydrogen is evolved in the electrolysis of soln. of cobalt sulphate, and R. Schildbach observed that from neutral soln. in an atm. of hydrogen, cobalt is deposited with quantitative current efficiency. The difference of potential between the electrode and the electrolyte is, however, much larger than the equilibrium value. The difference increases with the current density, and diminishes as the temperature rises, almost vanishing at 90°; it is very much increased by the addition of small quantities of acid to the solutions, and this effect is especially marked at low temp. M. J. Udy observed that in the electrolysis of soln. of cobalt sulphate, containing 0.3 to 1.0 per cent. of free sulphuric acid, the current efficiency is 80 to 95 per cent.; and with 5 per cent. of acid, about 8 per cent. The voltage required for soln. with up to 1 per cent. of free acid is 0.5 to 2.0 volts lower than it is with neutral soln. having the same current efficiency—there is a strong tendency for oxides to be formed on the anode. J. H. Paterson showed that with dil. soln., and low current densities there is a cathodic separation of hydroxide and hydrogen. M. M. Raessler's observations on the influence of composition, acidity, temp., and current density,  $D$ , amp. per sq. dm., at the cathode, on the deposition of cobalt are summarized in Table I.

TABLE I.—THE EFFECT OF VARIABLES ON THE DEPOSITION OF COBALT.

$N\text{-CoSO}_4$								
Normality of Acid	18°				75°			
	Voltage		Percentage Efficiency		Voltage		Percentage Efficiency	
	1.25 <i>D</i>	2.50 <i>D</i>	1.25 <i>D</i>	2.50 <i>D</i>	1.25 <i>D</i>	2.50 <i>D</i>	1.25 <i>D</i>	2.50 <i>D</i>
0.01	1.30	1.95	97.23	99.07	0.83	1.20	98.49	99.91
0.1	0.85	1.80	47.28	60.36	0.65	0.95	58.91	70.00
0.3	0.80	1.50	21.07	32.08	0.60	0.90	39.69	52.57

$N\text{-CoSO}_4 + 0.1N\text{-H}_2\text{SO}_4$						
<i>D</i>	18°		55°		75°	
	Voltage	Percentage Efficiency	Voltage	Percentage Efficiency	Voltage	Percentage Efficiency
0.625	1.10	28.14	0.65	57.55	0.55	68.05
1.250	1.60	51.44	0.95	69.57	0.85	79.16
2.500	2.60	63.73	1.55	80.55	1.32	82.24

The preparation of cobalt by electrolysis has not developed very far industrially. The subject was discussed by H. T. S. Britton, J. L. G. de Burlet, E. B. Cutten, N. H. M. Dekker, V. Engelhardt, C. Hoepfner, V. N. Hybinette, G. H. Montillon and N. S. Cassel, C. J. Reed, and M. J. Udy. C. J. Reed obtained an amalgam by

electrolysis with a mercury cathode, and removed the mercury by distillation. H. Moissan also obtained cobalt by distilling mercury from the amalgam. J. W. Beckmann electrolyzed a fused mixture of cobalt oxide and lime; and H. Skappel electrolyzed fused sulphide, or a mixture of sulphide and oxide.

H. Roehler electrolyzed soln. of cobalt chloride in formamide, but did not obtain deposits of the metal; but H. A. Pagel and O. C. Ames, and L. F. Yntema and L. F. Audrieth obtained a deposit with a soln. of cobalt acetate in formamide at 100°; and with a soln. of cobalt chloride in acetamide at 100°, but not with soln. of cobalt chloropentamminochloride or of potassium cobalticyanide in acetamide at 100°. H. S. Booth and M. Merlub-Sobel studied the deposition of cobalt from soln. of thiocyanate in liquid ammonia.

The deposition of cobalt for electrochemical analysis has been investigated by many. A. Classen recommended using a soln. of 0.3 grm. of cobalt sulphate, 4 to 5 grms. of ammonium oxalate made up to 120 c.c., and employing a current density of 1 ampere per sq. dcm. for 2.5 to 3.5 hrs. at 60° to 70°, and 3.1 to 3.8 volts. According to F. M. Perkin, the deposit is contaminated with a little carbon. H. Fresenius and F. Bergmann recommended as an electrolyte: 0.5 grm. of cobalt sulphate, 5 to 6 grms. of ammonium sulphate, and 40 c.c. aq. ammonia of sp. gr. 0.96 made up to 150 to 170 c.c., using 0.7 amp. at 20° to 25°; B. Neumann recommended: 1 grm. of cobalt chloride, 5 grms. of ammonium chloride, and 30 c.c. aq. ammonia made up to 150 c.c., using 1.5 amp. for 5 to 6 hrs.; E. F. Smith added 0.1 grm. more potassium cyanide to a soln. of a cobalt salt than is needed for precipitation and re-solution, along with 2 grms. of ammonium carbonate made up to 150 c.c., and using 1.5 amp. at 60° and 6.0 to 6.5 volts for 3.5 hrs. B. Neumann added that if the potassium cyanide is in excess, the separation of cobalt is incomplete. F. M. Perkin and co-workers recommended adding to a soln. of the cobalt salt, 2 c.c. of a 5 per cent. soln. of phosphoric acid, and 20 to 25 c.c. of a 10 per cent. soln. of sodium dihydrophosphate. The subject was studied by J. M. Albahary, D. Balachowsky, A. Brand, O. Brunck, E. D. Campbell and W. H. Andrews, M. S. Cheney and E. H. S. Richards, A. Classen and M. A. von Reis, O. Ducru, N. V. Emelianova, M. Engels, A. Fischer and co-workers, F. Förster, H. Fresenius and F. Bergmann, O. W. Gibbs, R. von Foregger-Greifenturn, V. Kohlschütter and F. Jakober, C. A. Kohn and J. Woodgate, C. Lucknow, Mansfeldsche Berg- und Hüttendirektion in Eisleben, E. Murmann, B. Neumann, H. Nissenson and H. Danneel, F. Oettel, W. Ohl, H. A. J. Pieters, O. Piloty, N. A. Puschin and R. M. Trechzinsky, A. Rosenheim and E. Huldskinsky, A. Riche, J. E. Root, G. A. le Roy, F. Rüdorff, L. Schlucht, C. P. Schweder, M. Schlötter, H. Thomälen, G. Vortmann, A. Waller, H. S. Warwick, and F. Wrightson. E. F. Smith and co-workers obtained good results with soln. containing formic acid, lactic acid, or a lactate. P. Bruylants, F. F. Exner, H. Fresenius and F. Bergmann, E. F. Smith and co-workers, B. Tougarinoff, and K. Wagemann used a rotating anode, with or without a mercury cathode, for the rapid precipitation of cobalt from soln. of the chloride or sulphate.

In 1842, R. Böttger<sup>3</sup> showed that metal could be coated with cobalt electrolytically. The similarities between cobalt and nickel are so great that much of the work which has been done on the electroplating of nickel can be applied to the electroplating of cobalt. This is the conclusion from the various writers—G. Langbein, A. Hollard and L. Bertiaux, A. Brochet, W. Pfanhäuser, W. G. McMillan and W. R. Cooper, A. Watt, S. P. Thompson, E. Brüant, W. Maigne and O. Mathey, and W. R. Barclay and C. H. Hainsworth. Several of the earlier soln. which were proposed, were based on that of A. C. and E. Becquerel indicated above. Thus, G. W. Beardslee used a soln. of 30 to 45 grms. of cobalt chloride per litre of water made faintly alkaline with ammonia; I. Adams, 22.5 grms. of cobalt chloride and 15 grms. of ammonium or magnesium chloride. E. D. Nagel employed a soln. of 400 parts of cobalt sulphate, and 200 parts of ammonium sulphate, dissolved in 6000 parts of distilled water mixed with 120 parts aq. ammonia of sp. gr. 0.909.

The soln. was employed at 38°. I. Adams also employed soln. of cobalt sulphate with ammonium or magnesium sulphate. A. Brochet also used a soln. of ammonium cobalt sulphate; and S. P. Thompson, either a soln. of 60 grms. of cobalt sulphate, 30 grms. of magnesium sulphate, and 60 grms. or less of ammonium sulphate; or a soln. of 100 grms. of ammonium cobalt sulphate, 50 grms. of magnesium sulphate, 6.2 grms. of citric acid, and 12.5 grms. of ammonium carbonate. W. Maigne and O. Mathey used a soln. of 28.6 grms. cobalt chloride, 14.3 grms. of potassium cyanide, and 143 grms. of sodium thiosulphate; or else a soln. of 20 grms. of cobalt chloride and 10 grms. of potassium thiocyanate. G. Langbein, and B. Neumann used a soln. of 40 grms. of ammonium cobalt sulphate and 20 grms. of boric acid. J. Vandermersch used a soln. of cobalt along with one of several acids—benzoic, salicylic, boric, gallic, pyrogallic, sulphurous, perchloric, formic, lactic, or acetic acid. M. Kugel recommended the addition of 1 to 10 grms. per litre of perchloric, perbromic or sulphuric acid at 30°. A. Classen used a hot soln. of 50 grms. cobalt sulphate, 80 grms. of ammonium oxalate, 20 grms. of potassium oxalate, and a litre of water. E. Placet and J. Bonnet specified the use of “bisulphate, biphosphates, and biacetates.” H. T. Kalmus and co-workers recommended 200 grms. of ammonium cobalt sulphate per litre for current densities up to 4 amps. per sq. dcm.; and 312 grms. cobalt sulphate, and 19.6 grms. sodium chloride per litre, and nearly saturating the soln. with boric acid for current densities between 3.5 and 26.4 amps. per sq. dcm. G. Fuseya and co-workers studied the effect of various additions to the bath.

A. Watt tried soln. of various kinds, and H. T. Kalmus and co-workers studied the subject. It was concluded that by the methods just indicated, cobalt can be deposited on to brass, iron, steel, copper, tin, lead, Britannia metal, and German silver, so as to give a firm adherent, hard, uniform surface which can be buffed and finished to give a white metal with a bluish cast, and possessing good lustre. The deposit of cobalt is harder than that of nickel, and it can be hammered, bent, or burnished as in the tests applied to nickel deposits. The electrical conductivity of the cobalt soln. is greater than is the case with ordinary nickel soln., and they can therefore be worked at a lower voltage for a given speed of plating.

Electroplating with cobalt was discussed by W. S. Barrows, A. C. and E. Becquerel, C. H. Buchanan and T. Haddom, B. Carr, Farbenindustrie Aktien Gesellschaft, M. Fiedler, C. Formenti and M. Levi, A. Gaiffe, T. H. Gant, B. Jirotko, P. R. Jourdain and A. R. Bernard, W. G. Knox, D. J. McNaughton and A. W. Hothersall, P. Marino, Q. Marino, C. P. Madsen, G. H. Montillon and N. S. Cassel, E. D. Nagel, A. Nefgen, A. Rosenberg, G. A. Roush, M. Schlötter, L. Schulte, O. Sprenger, F. T. Taylor, H. N. Warren, and E. Weintraub.

W. Guertler and G. Tammann<sup>4</sup> observed that the cobalt of commerce contained 2.22 per cent. nickel, 0.08 per cent. copper, 0.23 per cent. iron, and 0.04 to 0.06 per cent. of matter insoluble in acid, whilst the *cobaltum purissimum* of commerce had 1.62 per cent. nickel, 0.10 per cent. iron, and traces of copper. H. Copaux said that the cobalt of commerce contains sulphur, phosphorus, copper, aluminium, calcium, iron, and nickel; and in addition, S. P. L. Sørensen found lead, arsenic, zinc, manganese, alkaline earths, and silica. H. T. Kalmus found that cobalt reduced from commercial oxide contained 96.8 to 99.63 per cent. of cobalt; 0 to 0.65 per cent. of nickel; 0.56 to 2.36 per cent. of iron; 0.021 to 0.47 per cent. of sulphur; 0.062 to 0.24 per cent. of carbon; 0 to 0.06 per cent. of calcium; 0 to 0.14 per cent. of silica; and about 0.06 per cent. of manganese, 0.11 per cent. of arsenic; and 0.017 per cent. of phosphorus. H. Moissan's cobalt prepared in the electric furnace contained 0.733 per cent. of impurity. The subject was discussed by P. Georgi and G. Schnieder, C. Winkler, and W. Hessenbruch. A. Sieverts and W. Krumbhaar removed occluded gases by heating the metal to 1400°. B. Egeberg removed zinc by volatilization from the molten metal; C. Winkler, carbon, by heating the metal with cobalt oxide; B. Bogitch, sulphur,

by heating the metal with wood-charcoal; and P. Manhès, iron and sulphur, by fusion with alkali fluxes.

The melting and casting of cobalt were discussed by H. Copaux,<sup>5</sup> W. Hankel, C. Winkler, and S. B. Wright, for containing vessels—*vide supra*. The mechanical working of the metal was discussed by Berndorfer Metallwaarenfabrik, C. Brunner W. B. Clarke, H. Copaux, P. G. Ehrhardt, T. Fleitmann, P. Georgi and G. Schnieder, H. T. Kalmus, P. McCorkle, E. Maurer, P. F. Monnot, G. Selve and F. Lotter, A. Valenciennes, and C. Winkler. T. Fleitmann prepared **malleable cobalt** by adding magnesium to the molten metal as described for nickel (*q.v.*). S. Kaya obtained **single crystals of cobalt** several c.c. in vol. from 99.8 per cent. electrolytic cobalt, by cooling molten cobalt extremely slowly when the metal is in the vicinity of its transition temp. Many processes of reduction of cobalt salts in aq. soln., the reduction of the oxide by hydrogen, and distillation of the amalgam, and the thermal decomposition of the carbonyl, furnish **pulverulent cobalt**. A. Estelle also obtained a fine powder by the electrolysis of a neutral salt of cobalt mixed with a hydroxylic organic compound—sugar or glycerol. G. Magnus prepared **pyrophoric cobalt** by reducing the oxides in a current of hydrogen. H. Moissan added that the best temp. for reduction is about 250°; if the metal is reduced at 700°, or obtained by distilling the amalgam, it is not pyrophoric. N. Nikitin also found that the oxalate reduced between 275° and 350° is not pyrophoric, but if the oxalate is previously triturated alone or mixed with less than 50 per cent. of manganous oxalate and heated to 330° to 350°, it furnishes pyrophoric cobalt. C. Winkler, and B. Kerl said that when cobalt oxide is reduced with ammonia so that it contains 14 to 16 per cent. of oxygen, it glows when exposed to air. Pyrophoric cobalt is a black powder which burns brilliantly when exposed to air in consequence of rapid oxidation.

A. Kundt, H. Bracchetti, L. R. Ingersoll, J. Strong and C. H. Cartwright, W. Lobach, A. Skinner and A. G. Tool, E. Breuning and O. Schneider, R. M. Bozorth, E. Hirsch, V. Kohlschütter and F. Jakober, and E. P. T. Tyndall and W. W. Wertzbaucher discussed the preparation of **cobalt mirrors** electrolytically—*vide* iron mirrors; A. Skinner and A. G. Tool, E. O. Hulburt, and J. D. Hanawalt and L. R. Ingersoll, by cathodic spluttering; A. Knocke, J. C. Steinberg, and A. J. Sorensen, by the evaporation of cobalt, which begins in vacuo at about 640°; W. Spring, by the reduction of the vapour of cobalt chloride with hydrogen; and F. K. Richtmyer and F. W. Warburton, by reducing the oxide, composed to a thin layer, with hydrogen. T. A. Edison, and H. C. Hubbell prepared films of oxidation and reduction, and treated them with dil. acids to remove iron, and arsenic; the resulting surfaces were said to be very active chemically. G. F. Taylor obtained **cobalt filaments** by drawing the molten metal enclosed in a suitable quartz-glass tube, and afterwards removing the glass with hydrofluoric acid.

F. Ehrenhaft,<sup>6</sup> and O. Scarpa prepared **colloidal cobalt** by electrical spluttering under water by G. Bredig's method—3. 23, 10—and T. Svedberg added that the product was probably a colloidal hydroxide or oxide. T. Svedberg prepared the colloid by an oscillating discharge—3. 23, 10. C. Benedicks, D. Zavrieff, A. H. Erdenbrecher, and J. Billitzer also prepared the colloid by electrical spluttering. The Chemische Fabrik von Heyden obtained the colloid by electrical spluttering in the presence of a reducing agent, and a protective colloid, and found that with 0.03 per cent. of cobalt, the sol is very dark brown, almost black in reflected light, and dark brown in transmitted light. A. Pieroni and E. Girardi reduced pyridine soln. of cobalt salts by a soln. of pyrogallol, pyridine, and diluted the mixture with water—if cobalt acetate is used, the dilution with water is not necessary. C. Paal, and C. Paal and H. Boeters obtained the hydrosol by reducing a hydrosol of cobalt hydroxide in the presence of a hydrosol of palladium—with sodium protalbate or lysalbate as protective colloid. H. H. Franke used gum arabic, gelatin, gum tragacanth, saponin, and sodium lysalbate as protective colloid, and hydrazine, or a salt of hydrazine, in the presence of alkali, as reducing



agent. The hydrosol or hydrogel is reversible. L. Hugounenq and J. Loiseleur used glycogen as protective colloid. A. Job and R. Reich obtained a colloid by the action of ethylmagnesium bromide on cobalt iodide in benzene. H. Nordenson said that colloidal cobalt is not formed by the action of ultra-violet light, or X-rays, or radium rays on cobalt in contact with water or other dispersion media. The oxidizable metals yield hydrated oxides, and the action of these radiations is to accelerate changes which occur in their absence. T. Svedberg prepared **alcosols** by oscillatory sparking under isobutyl or ethyl alcohol as dispersive medium. A. Lesure obtained a colloidal suspension in oil for intramuscular injections.

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## § 6. The Physical Properties of Cobalt

The cobalt obtained by the reduction of the oxide in hydrogen, is a grey or black powder. A. A. Valenciennes<sup>1</sup> said that the metal *en masse*, after it has been fused, has the colour of polished iron; whilst H. T. Kalmus and co-workers said that its colour is like that of nickel, although, when plated and polished, it is silver-white with a slight bluish tinge. C. Brunner, W. A. Lampadius, P. Georgi and G. Schneider, H. Nagaoka and K. Honda, and H. Copaux also said that the metal is silver-white, and C. Winkler, that it is bluish-white or greyish-white like zinc. Sometimes cobalt appears as a black matte. According to A. W. Wright, a thin film of cobalt in transmitted light appears grey or brownish-grey; and G. T. Beilby said blue. P. Berthier said that the metal has a fracture like that of cast-iron. E. van Aubel discussed the colour and transparency of thin films of cobalt.

H. T. Kalmus and co-workers,<sup>2</sup> R. Vogel, R. Ruer and K. Kaneko, and K. Friedrich observed that deep etching shows massive cobalt to contain polyhedral crystals. R. Ruer and K. Kaneko observed twinning in the crystals of cast cobalt, and R. Vogel added that twinning is an effect of cold-work, and vanishes when re-crystallization occurs during annealing. R. Vogel observed Neumann's lines; G. Tammann and Q. A. Mansuri, the re-crystallization of cobalt; F. Sauerwald, the grain-growth during sintering; G. Quincke, the formation of what he called foam-cells during the solidification of the molten metal; and R. M. Bozorth, and R. Vogel, the orientation of the crystals. Cobalt is dimorphous in that it forms a variety with hexagonal crystals stable at ordinary temp., and a variety with cubic crystals stable above 400°, although both forms may be present in ordinary cobalt. S. B. Hendricks and co-workers said that cobalt has a hexagonal lattice above 1015° and below 400°, and in between, a cubic lattice. H. Perltz studied the

distance apart of the atoms. G. T. Beilby observed that the polished metal has a transparent, glass-like film which may pass into minute scales or granules. H. Kersten, R. M. Bozorth, F. Bitter, and V. Kohlschütter and F. Jakober studied the structure of the electro-deposited metal.

A. W. Hull observed that the **X-radiograms** of electro-deposited cobalt correspond with a close-packed, hexagonal lattice—Fig. 2—with the side of the

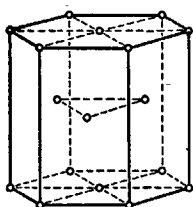


FIG. 2.—Close-packed, Hexagonal Lattice of Cobalt.

elementary, triangular prism  $c=2.514$  Å., and the distance between the nearest atoms,  $a=2.514$  Å., or  $a:c=1:1.633$ ; S. Sekito gave  $a=2.498$  Å.,  $c=4.052$  Å., and  $a:c=1:1.622$ ; A. Osawa gave  $a=2.492$  Å.,  $c=4.056$  Å., and  $a:c=1:1.63$ ; and F. Wever and U. Haschimoto,  $a=2.514$  Å.,  $c=4.17$  Å., and  $a:c=1:1.66$ . A. W. Hull observed that filings of the metal, after being heated in hydrogen to  $600^\circ$  for 6 hrs., possessed a mixture of cubic and hexagonal lattices in about equal proportions. It was not possible by annealing to complete the transformation from the hexagonal to the cubic form, but by reducing the oxide in hydrogen at  $600^\circ$ , the metal had a face-centred, cubic lattice of side  $a=3.554$  Å., and a distance of  $2.514$  Å. between the nearest atoms. S. Sekito found for the cubic lattice  $a=3.558$  Å.; F. Wever and U. Haschimoto,  $a=3.554$  Å.; A. Osawa,  $a=3.525$  Å.; and L. Vegard and H. Dale,  $a=3.533$  Å. H. Kahler, E. A. Owen and E. L. Yates, A. Karlsson, H. Shoji, S. B. Hendricks and co-workers, H. Masumoto, R. W. G. Wyckoff, and E. C. Bain discussed this subject. L. R. Ingersoll and J. D. Hanawalt found that a cobalt film spluttered in nitrogen is metallic and non-magnetic; it has a face-centred, cubic lattice, with  $a=4.297$  Å., and this reduces to the normal, face-centred, cubic lattice with  $a=3.554$  Å., when it is degassed and crystallized at  $400^\circ$ ; and H. Kahler observed that a film obtained by cathodic spluttering had a regular orientation of crystallites of both cubic and hexagonal forms. G. Sachs studied the effect of mechanical work on the lattice; and W. H. Rothery, the relations amongst the lattice constants of cobalt and other metals.

From a study of the gold-cobalt alloys, W. Wahl<sup>3</sup> inferred that above  $1400^\circ$ , cobalt forms cubic crystals, and below that temp., hexagonal crystals. H. Pechaux also considered that two breaks in the thermoelectric curve of cobalt at  $280^\circ$  and  $550^\circ$  represent **allotropic transformations**. K. Konda and S. Shimizu observed discontinuities in the effect of temp., on the magnetization of cobalt, and inferred that there is a transition temp., or change of phase at  $464^\circ$ . It is now known that cobalt exists at ordinary temp. in a form,  **$\alpha$ -cobalt**, with a stable, close-packed, hexagonal lattice, and that at the **transition temperature**, about  $400^\circ$ , it furnishes  **$\beta$ -cobalt**, the stable form above  $400^\circ$ , and possessing a face-centred, cubic lattice. Both forms may exist side by side at ordinary temp., but  $\alpha$ -cobalt is the stable form,  $\beta$ -cobalt the unstable form. U. Dehlinger and co-workers discussed the mechanism of the transformation and inferred that a single crystal suffering an allotropic transformation does so by a simple shearing movement of the atoms on that atom plane of the proper family of planes which will produce the smallest increase in the surface area of the crystal.

A. Schulze observed that the temp. coeff. of the electrical resistance of cobalt of a high degree of purity remains nearly constant between  $444^\circ$  and  $467^\circ$ ; and that the reverse transformation is completed at about  $350^\circ$ ; with cobalt containing 0.47 per cent. of iron, the transformation temp. is between  $403^\circ$  and  $446^\circ$ , and the reverse transformation is completed at  $150^\circ$ . Measurements of the thermal expansion indicate a transformation between  $451^\circ$  and  $452^\circ$ , and the reverse transformation ends at about  $100^\circ$ . Measurements of the thermoelectric force against platinum indicate a transformation between  $456^\circ$  and  $470^\circ$ . A. Schulze gave  $444^\circ$  for the transition temp.; S. B. Hendricks and co-workers gave  $400^\circ$ ; G. Wassermann,  $450^\circ$ ; S. Umino,  $460^\circ$ ; and P. H. Emmett and J. F. Schultz between

340° and 360°—but this last result is too low. H. Masumoto observed that the effect of impurities on the transformation temp. is irregular when determined by observations on the thermal expansion, thermal effects, electrical resistance, or magnetization. Both forms are ferromagnetic, and the transformation exhibits an hysteresis being much lower on a falling temp. than it is on a rising temp. With cobalt of the highest degree of purity, and with the following percentage proportions of iron—other impurities in brackets—the observed transformation temp. were :

Impurities	.	.	0	0.04 (0.189)	0.10 (0.162)	0.33 (0.086) per cent.
Transition	{	Heating	477°	447°	442°	427°
		Cooling	403°	400°	400°	360°

S. B. Hendricks and co-workers observed that  $\beta$ -cobalt appears when cobaltous oxide is reduced in hydrogen above 400°, and after standing 7 months, it shows no sign of the presence of  $\alpha$ -cobalt; but the cast metal, and cobalt reduced from cobaltous oxide by hydrogen above 1015° has the close-packed hexagonal lattice of  $\alpha$ -cobalt. The cubic form is therefore stable between 400° and 1015°. According to A. W. Hull, a sample of 99.7 per cent. cobalt gave an X-radiogram consisting only of  $\alpha$ -cobalt; and after heating for about 6 hrs. at 600° in hydrogen, it contained about equal proportions of  $\alpha$ - and  $\beta$ -cobalt; it was not possible to obtain a complete transformation into  $\beta$ -cobalt at this temp. Cobalt obtained from the oxide reduced by hydrogen at 600° consists of  $\beta$ -cobalt, and only traces of  $\alpha$ -cobalt. The electrolytic metal contains about equal parts of the two forms, whereas S. Sekito found that the electrolytic metal often contains only  $\alpha$ -cobalt. S. Kaya found that a slowly-cooled sample, with 0.116 per cent. of iron, and 0.0924 per cent. of other impurities, consisted entirely of  $\alpha$ -cobalt; and A. B. Cardwell observed commercial samples of 99.9 per cent. cobalt sometimes contained  $\beta$ -cobalt, and other samples not so. M. R. Andrews observed that alloys with 100 to 5 per cent. of iron had the cubic lattice; alloys with 2 per cent. of iron had the cubic lattice and faint signs of the hexagonal lattice, and cobalt alone had the hexagonal lattice. A. Rogers found that electrolytic cobalt previously heated to 500°, had a transition temp. of 420° and when melted in vacuo, and heated to 1100°, the transition temp. was 445°. F. Wever and U. Haschimoto attributed the variations in the determinations of the transition temp. as due to strong hysteresis, and to the presence of different proportions of the two allotropes in the metal prepared in different ways. C. L. Utterback observed an irregularity in the total reaction of cobalt between 1047° and 1107° corresponding with the Curie point.

The transformation was shown by H. Masumoto, W. C. Ellis, and S. B. Hendricks and co-workers to be influenced by strong magnetic fields. According to A. B. Cardwell, in the intermediate stages of the transformation the photoelectric and thermionic sensibilities are augmented; and he believes that the purified metal, thoroughly free from occluded gases, will have a higher transition temp. than that usually accepted. For the energy changes during the transformation, *vide infra*.

Both  $\alpha$ - and  $\beta$ -cobalt are ferromagnetic, and H. Masumoto found that cobalt becomes paramagnetic at 1100°. This, the Curie temperature, corresponds with the  $A_2$ -arrest of iron at 790°, and with nickel, at 380°. S. Umino gave 1150° for the Curie temp., and A. Schulze, 1128°—*vide infra*. There is a doubt whether the temp. of magnetic transformation is connected with a change of phase. G. Wassermann observed no allotropic transformation point at 10° to 15°. W. Guertler and G. Tammann, and R. Ruer and K. Kaneko considered that there is also a polymorphous change at the Curie temp. H. Masumoto, however, said that there is no change of phase, or of atomic arrangements. S. N. Hendricks and co-workers also said that there is no change in the lattice constant at the Curie temp., 1103°, although there is a transformation temp. at 1015°—*vide supra*. A. Schulze said that the curves of electrical resistance, and thermoelectric force against platinum change their direction at 1128°, but there is no abrupt change as usually occurs with changes of phase.

T. Bergman<sup>4</sup> gave 7.7 for the **specific gravity**, but his metal was impure, and the datum was too low; J. J. Berzelius gave 8.5131; C. Brunner, 8.485; B. M. Tassaert, 8.5385; S. Bottone, 8.5 at 15.5°; R. J. Häuy, 8.5384; W. A. Lampadius, 8.7; T. H. Henry, 8.558; and L. Playfair and J. P. Joule, 7.718 to 8.260; C. F. Rammelsberg gave for the reduced metal, 8.132 to 9.495—mean, 8.57. These observations, and those by F. A. C. Gren, were made before chemists had learned to purify the metal adequately. For the metal which had been fused, W. A. Tilden gave 8.718 at 21°/4°; G. Neumann and F. Streintz, and R. von Dalwitz-Wegner, 8.6; O. Block, 8.920; H. Copaux, 8.8 at 15°/4°; A. Schulze, 8.79 at 20°; and C. Winkler, for electrolytic cobalt foil, 7.9678 at 20°. T. M. Lowry and R. G. Parker gave 8.7706 for the metal in bulk, and 8.7453 for the cold-worked metal (filings). H. T. Kalmus and C. H. Harper found for 99.9 per cent. metal, cast from just above its m.p., about 1500°, 8.7562 at 15°; for the metal cast and swaged down to a thin cylindrical bar, 8.9227, at 19°; and for the cast metal, annealed at 700°, 8.8105 at 19°. A. W. Hull calculated for both the hexagonal forms a sp. gr. of 8.66, when the best representative value for ordinary cobalt is 8.8; S. Sekito similarly calculated 8.89 for  $\alpha$ -cobalt and 8.64 for  $\beta$ -cobalt. J. A. Groshans discussed some relations of the density of cobalt. For cobalt reduced from the oxalate by hydrogen, W. Biltz and W. Holverscheidt observed 8.83 at 25°/4°, and for the **atomic volume**, 6.68. I. I. Saslawsky, and E. Moles studied the at. vol.; and W. Biltz and K. Meisel calculated 6.58 for the at. vol. at absolute zero. The subject was studied by I. I. Saslawsky, and A. Heydweiller. E. Donath and J. Mayrhofer, I. Traube, and P. Niggli made observations on some relations of the at. vol. T. Barth and G. Lunde calculated from the lattice dimensions of the cubic form of cobalt the at. vol. 6.84, a value which lies between that of the cubic, face-centred forms of iron (7.11) and of nickel (6.53). F. Ephraim's relation between the dissociation temp.,  $T^\circ$  at 500 mm., and the at. vol.  $v$ , namely  $T^{1/3}v^{1/3}=14.0$ , furnishes 6.8. A. W. Hull, W. P. Davey, and J. K. Morse gave 1.257 Å. for the **atomic radius**; W. F. de Jong and H. W. F. Willems, 1.27 Å. to 1.29 Å.; and V. M. Goldschmidt, 1.26 Å. W. L. Bragg gave 1.37 Å. for the **ionic radius**. A. M. Berkenheim, M. L. Huggins, H. Grimm, E. Piwowarsky, P. Röntgen and W. Koch, E. Herlinger, E. J. Cuy, V. M. Goldschmidt, L. Pauling, P. Walden, R. G. Lunn, A. Ferrari and F. Giorgi, E. H. Westling, J. C. Slater, and E. T. Wherry made observations on this subject from which it follows that for trivalent cobalt, the effective at. radius is 0.29 to 0.47 Å.; for bivalent cobalt, 0.72 to 0.82 Å.; and for neutral cobalt atoms, 1.26 to 1.39 Å. G. Natta and L. Passerini found that if the radius of oxygen is 1.32 Å., that of cobalt is 0.80 Å.; and G. Natta and A. Reina gave 2.92 Å. for the diameter of the  $\text{Co}^{++}$ -ion. The subject was also discussed by V. M. Goldschmidt, G. Berg, A. F. Scott, H. Grimm, and O. E. Frivold. M. Toepler found that on melting, a gram of cobalt expands 0.0064 c.c. or 5.2 per cent. K. Honda and co-workers gave 2.03 per cent. for the expansion during the solidification of cobalt with 2.2 per cent. of carbon. A. Kapustinsky discussed the effect of solvation on the ionic radius.

J. B. Dumas observed that cobalt is scratched by glass of hardness 5.6 on Mohs' scale. S. Bottone gave for the **hardness** of cobalt 0.145, when that of nickel is 0.141, that of silver, 0.099, and that of the diamond, 0.300. S. F. Scherut-schuschny and S. W. Belynsky gave 4, and H. Copaux gave 5.5 on Mohs' scale. T. Turner, and E. van Aubel said that cobalt is harder than iron. T. Turner found that the hardness of cobalt is 1450 when that of nickel is 1410; that of iron, 1375; and that of the diamond is 3010. M. Waehlert gave 136 for Brinell's hardness; and C. A. Edwards, 86.0. R. Ruer and K. Kaneko estimated that Brinell's hardness of cobalt is 132; and H. T. Kalmus and C. H. Harper found that the hardness of 99.9 per cent. cobalt, cast from just above its m.p. with a load 3400 lbs., is 124; the values for cast and sheet nickel are 83.1 and 85.1 respectively. Hence the hardness of cobalt cast from just above its m.p. is higher than that of iron or nickel cast under similar conditions. If commercial cobalt has 0.060 to 0.37 per cent. of carbon, the

increased hardness is not sufficient to affect variations due to heat-treatment. D. J. McNaughton, and D. J. McNaughton and A. W. Hothersall found that the Brinell's hardness of electro-deposited cobalt varies from 270 to 311; and L. Guillet and J. Cournot found that by immersion in liquid air, the hardness rose from 174 to 222 on Brinell's scale. E. Maurer said that by cold-working, involving a 3 per cent. extension, the hardness of cobalt with 4.15 per cent. of nickel rose from 180 to 280. M. Guichard and co-workers said that the hardness is independent of the hydrogen content.

The early observers—*e.g.*, P. Berthier, E. S. Clarke, and C. Brunner—noted that cobalt is malleable under the hammer. H. T. Kalmus and C. H. Harper observed that purified cobalt can be readily machined in a lathe, although it is somewhat brittle, and yields a short chip. The addition of a small proportion of carbon renders the metal less brittle, for it then yields a longer curling chip when turned. Purified cobalt cast in iron or sand moulds, slowly or rapidly cooled, cannot be directly swaged down to fine wire without special heat-treatment; but commercial cobalt, containing small percentages of carbon, can be readily swaged down from cast bars to wires of any desired diameter.

Observations on the **tensile strength** of cobalt were reported by H. St. C. Deville. The value for purified cobalt, cast and unannealed, is nearly 34,400 lbs. per sq. in. T. H. Gant gave 15.35 tons per sq. in. If the metal be annealed, the tensile strength is only slightly increased, the average value is 36,980 lbs. per sq. in. H. Copaux found the tensile strengths of iron, nickel, and cobalt to be respectively 23,000, 18,000, and 60,000 lbs. per sq. in. R. Ruer and K. Kaneko gave 25 kgrms. per sq. mm. for the tensile strength of cobalt. P. W. Bridgman gave 39.7 kgrms. per sq. mm. for the breaking stress of a wire of 0.0762 mm. diameter and annealed at a red-heat. H. T. Kalmus and co-workers observed that the percentage reduction in area, and the elongation are small for purified cast cobalt. The tensile yield-point is generally very close to the tensile breaking load. The tensile strength of cobalt increases rapidly as the metal is rolled, and it may attain 100,000 lbs. per sq. in. by being swaged down to wire. The effect of carbon is to raise the tensile strength from 34,400 lbs. per sq. in. for cast and unannealed metal to 61,000 lbs. per sq. in. for cobalt with 0.060 to 0.30 per cent. of carbon. The average value for 0.062 per cent. of carbon is 59,700 lbs. per sq. in., and for 0.25 per cent. of carbon, 61,900 lbs. per sq. in. The effect of carbon and other impurities in commercial cobalt is greatly to increase the percentage elongation and reduction of area, which rise in most cases well over 12 per cent.

H. T. Kalmus and C. H. Harper found that the **compressive strength** of purified cobalt, cast and unannealed, is about 122,000 lbs. per sq. in. The effect of annealing is not very marked, being near 117,200 lbs. per sq. in., so that annealing has a tendency to lower the compressive strength. The compressive yield-point of annealed and purified cobalt is 56,100 lbs. per sq. in. compared with 42,200 lbs. per sq. in. for unannealed cobalt, so that the yield-point is slightly raised by annealing. The compressive strength of purified cobalt cast just above its m.p., cooled in an iron mould, and machined in a lathe to test-bar size, is much greater than the corresponding values for iron and nickel. The effect of the presence of carbon, as in commercial cobalt, is to increase the compressive strength above 175,000 lbs. per sq. in. for the addition of 0.060 to 0.30 per cent. of carbon. The yield-point is not greatly affected, but it is lowered from 5 to 10 per cent. for 0.060 to 0.30 per cent. of carbon for both annealed and unannealed metal. The effect of annealing commercial cobalt is to lower its compressive strength—*e.g.*, unannealed specimens gave 183,000 lbs. per sq. in., and annealed samples 140,000 lbs. per sq. in. The compressive yield-point of commercial cobalt is similar to that of the purified metal, being 39,000 lbs. per sq. in. for unannealed samples, and 53,000 lbs. per sq. in. for annealed samples.

K. Honda gave  $E=2.038 \times 10^{12}$  for Young's **elastic modulus** of 97.12 per cent. cobalt; and H. Tomlinson gave  $E=2.005 \times 10^{12}$  for unannealed



cobalt, and  $E=1.817 \times 10^{12}$  for the annealed metal. E. Widder gave  $E=E_{20}\{1-0.0006803(\theta-20)\}$ . H. Walker obtained, at different temp.:

	11.2°	35°	78°	100°	130°
$E \times 10^{12}$	1.479	1.476	1.475	1.473	1.471

K. Honda and co-workers studied the effect of magnetization, and observed that with a wire 64 cm. long, and 1 cm. diameter, in a magnetic field of  $H$  gauss:

$H$ $dE/E$	Load = 1005 grms.			Load = 2830 grms.		
	100	250	500	100	250	500
	0.0025	0.0053	0.0077	0.0088	0.0028	0.0043

K. Honda observed for 97.12 per cent. cobalt the **torsion modulus** or **rigidity**  $n=7.63 \times 10^{11}$  to  $7.71 \times 10^{11}$ ; E. Drago,  $9.00 \times 10^{11}$ ; and W. Sutherland gave 18,200 kgrms. per sq. mm. The effect of cooling near  $-110^\circ$  was studied by L. Guillet and J. Cournot. K. Honda and co-workers observed for the effect of a magnetic field of  $H$  gauss:

$H$	100	200	400	600	800
$dn/n$	0.0005	0.0012	0.0021	0.0028	0.0031

P. W. Bridgman found the **compressibility** of purified cobalt at  $30^\circ$  to be  $v/v_0 = -(5.39-2.1 \times 10^{-5}p)p \times 10^{-7}$ , and at  $75^\circ$ ,  $v/v_0 = -(5.47-2.1 \times 10^{-5}p)p \times 10^{-7}$ . T. W. Richards found the mean change in vol. by 0.987 atm. press. is 0.27. P. W. Bridgman estimated the coeff. of compressibility to be  $\beta=0.0650$ ; and L. H. Adams gave  $\beta=0.0655$ , and for  $\beta/p$ ,  $-0.0114$ . T. W. Richards gave 510 kilomegabars, and R. F. Mehl, 510 kilomegabars for the **internal pressure**; and for the maximum disruptive internal press., 1870 kgrms. per sq. mm. T. W. Richards gave 329,000 megabars for the internal press. G. A. Tomlinson discussed the nature of the cohesive press. R. von Dallwitz-Wegner gave 338,670 atm. for the cohesion press. at  $0^\circ$ , and 305,728 atm. at  $100^\circ$ . E. Drago studied the internal friction of cobalt wires. J. F. Chittum studied the **surface energy**.

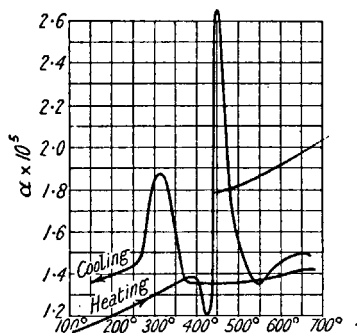
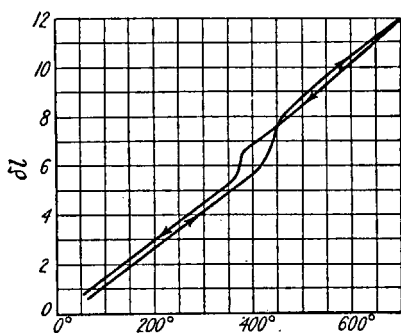
W. F. Barrett<sup>5</sup> found that the **velocity of sound** in cobalt is 14.2 (air unity); and A. Masson gave 4724.4 metres per second.

H. Fizeau<sup>6</sup> found the coeff. of **thermal expansion** of compressed cobalt, reduced by hydrogen, to be 0.041236 at  $40^\circ$ , and 0.041244 at  $50^\circ$ . A. Quadrio-Curzio gave 0.04181 between  $25^\circ$  and  $300^\circ$ ; and H. Masumoto and S. Nara, 0.041279 between  $30^\circ$  and  $100^\circ$ . E. P. Harrison gave for the value of  $\alpha$  between  $0^\circ$  and  $300^\circ$ ,  $\alpha=(1280+0.75\theta+0.0035\theta^2) \times 10^{-8}$ . A. E. H. Tutton gave  $\alpha=0.041208+0.07128$  between  $6^\circ$  and  $121^\circ$ . Observations were also made by E. van Aubel. R. von Dallwitz-Wegner gave for the coeff. of cubic expansion, 0.04362 at  $0^\circ$ , and 0.04401 at  $100^\circ$ . W. F. Barrett observed that an abrupt expansion occurs at a stage in the cooling of an incandescent wire. A. Schulze observed that the coeff. of thermal expansion of technically pure cobalt between  $0^\circ$  and  $20^\circ$ ,  $100^\circ$ ,  $300^\circ$ , and  $400^\circ$  are respectively 0.041255, 0.041357, 0.041437, and 0.041511. There is a sudden expansion between  $451^\circ$  and  $452^\circ$  due to a transition point, and on cooling, the transition is delayed to temp. as low as  $100^\circ$ . H. Masumoto found that the thermal expansion of one sample of cobalt has an abrupt change at  $442^\circ$ , and at  $427^\circ$  and  $477^\circ$  in other samples; and on cooling there is an abrupt contraction at  $360^\circ$  to  $403^\circ$ —Fig. 3. These changes correspond with an allotropic change in the metal which occurs at  $447^\circ$  on the heating curve, and at  $403^\circ$  on the cooling curve. The presence of iron or other impurities lowers the transition temp. F. L. Uffelmann's values of the coeff. of thermal expansion on heating and cooling curves are indicated in Fig. 4. G. A. Tomlinson discussed some interatomic relations of the thermal expansion; T. W. Richards, the relation between the inner press. and the coeff. of thermal expansion; and A. Denizot, the relation between the sp. ht. and compressibility and the coeff. of thermal expansion. T. M. Lowry and R. G. Parker observed a slight permanent contraction after annealing cobalt filings at  $100^\circ$ .

W. F. Barrett found that the **thermal conductivity** of cobalt is 0.172 when that

of silver is unity. According to K. Honda, the thermal conductivity of cobalt is 0.1653 cal. per degree per cm. per sec. at 30°; and H. Masumoto gave 0.1299 cal. per degree per cm. per sec. at 30°.

P. L. Dulong and A. T. Petit<sup>7</sup> gave 0.1067 for the **specific heat** of cobalt. H. V. Regnault gave 0.10674 for the sp. ht. of cobalt between 14° and 97°; and for



FIGS. 3 and 4.—The Thermal Expansion of Cobalt.

other samples, 0.10094 to 0.10727. W. F. Barrett gave 0.1070 between 15° and 100°; A. de la Rive and F. Marcet, 0.1172 between 5° and 15°; and W. A. Tilden found for temp. between 15°:

	−182°	−78°	100°	185°	350°	435°	550°	630°
Sp. ht.	0.0822	0.0939	0.1030	0.1047	0.1087	0.1147	0.1209	0.1234

and S. Umino gave for the mean and true sp. hts. of cobalt, the following results:

	100°	200°	300°	400°	450°	500°	600°	800°	900°	1000°
Mean.	0.1089	0.1107	0.1124	0.1145	0.1160	0.1185	0.1214	0.1298	0.1337	0.1378
True .	0.110	0.114	0.118	0.128	0.135	0.135	0.140	0.160	0.170	0.181
	1100°	1150°	1200°	1250°	1300°	1350°	1400°	1520°	1550°	1570°
Mean.	0.1420	0.1455	0.1480	0.1503	0.1527	0.1562	0.1579	0.2067	0.2079	0.2083
True .	0.199	0.213	0.203	0.208	0.213	0.219	0.225	0.265	0.265	0.265

The results are plotted in Fig. 5. There is a transformation point at 470°, and the ferromagnetic transformation at a higher temp., so that the curve has two maxima.

In the paramagnetic range, the sp. ht. curve is almost linear up to the m.p. The true sp. ht. of the molten metal does not vary with temp. H. E. Schmitz gave 0.0840 for the sp. ht. of cobalt between the b.p. of oxygen and 0°, and 0.10795 between 0° and 100°; H. Schimpff, 0.1030 between 17° and 100°; 0.0942 between 17° and 79°, and 0.0818 between 17° and −190°; T. W. Richards and F. G. Jackson, 0.828 between 19.6° and −185.9°; H. Copaux, 0.104 between 20° and 100°; and J. Pionchon gave 0.145063 at 500°; 0.184556 at 800°; and 0.204 at 1000°; and for the true sp. ht.,  $c$ , at 0° and 890°,  $c = 0.10584 + 0.0457334\theta + 0.07658281\theta^3$ ; and between 890° and 1150°,  $c = 0.124 + 0.00008\theta$ . P. Schübel gave 0.1042 between 18° and 100°, and 0.1220 between 18° and 600°; H. T. Kalmus and C. H. Harper, 0.1053 between 15° and 100°; A. Göbl, 0.0933 between 0° and −79°; 0.1041 between 0° and 100°; 0.1279 between 0° and 800°; and 0.1455 between 0° and 1187°; T. W. Richards and F. G. Jackson, 0.0828 between 20° and −188°; and J. Dewar, 0.0207 between −196° and −253°. The **atomic heat** thus ranges from 1.22 in the vicinity of −253° to 8.58 in the vicinity of 1187°.

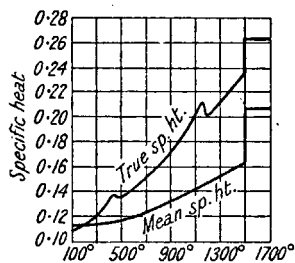


FIG. 5.—The Specific Heat of Cobalt.

H. E. Schmitz gave 4.96 at  $-85^{\circ}$ , and 6.37 at  $60^{\circ}$ . I. Maydell gave for the at. ht.  $A=8.720-938.9(\theta+352)^{-1}$ . E. D. Eastman and co-workers calculated  $C_p-C_v=0.13$  cal. per degree per mol. G. Tammann and A. Rohmann found for the heat capacity,  $-C_{100}$  cal. per gram-atom between :

	$-200^{\circ}$ to $-100^{\circ}$	$-100^{\circ}$ to $0^{\circ}$	$0^{\circ}$ to $100^{\circ}$	$100^{\circ}$ to $200^{\circ}$	$200^{\circ}$ to $300^{\circ}$	$300^{\circ}$ to $400^{\circ}$	$400^{\circ}$ to $500^{\circ}$
$C_{100}$	451.71	536.04	612.40	641.59	656.93	681.10	705.87

Observations were made by P. Oberhoffer and W. Grosse, F. Simon and M. Ruhemann, F. Wüst and co-workers, and J. F. Shadgen. J. R. Ashworth studied the relations between the thermal and magnetic constants of cobalt; A. H. Stuart, the relations between the elastic constants and the sp. ht.; G. A. Tomlinson, some interatomic relations of the sp. ht.; J. Perry, relations with the at. wts.; W. M. Latimer, and E. D. Eastman and co-workers, the thermal energy and the electrons; and J. Dorfmann and R. Jaanus, the change in the sp. ht. at the Curie point.

According to R. Pictet,<sup>8</sup> cobalt has a **melting-point** of  $1500^{\circ}$ ; T. Carnelley, and P. H. van der Weyde,  $1800^{\circ}$ ; W. Guertler and G. Tammann,  $1505^{\circ}$  to  $1528^{\circ}$ ; H. Copaux,  $1530^{\circ}$ ; E. M. Terry,  $1485^{\circ}$ ; G. K. Burgess,  $1464^{\circ}$  for 99.95 per cent. cobalt; G. K. Burgess and R. G. Waltenburg,  $1477^{\circ}$  to  $1478^{\circ}$ ; A. L. Day and R. B. Sosman,  $1489.8^{\circ}$ ; W. R. Mott,  $1489.8^{\circ}$ ; U. Raydt and G. Tammann,  $1480^{\circ}$ ; K. Hiege,  $1525^{\circ}$ ; J. Jahn,  $1565^{\circ}$ ; H. T. Kalmus and C. H. Harper,  $1478^{\circ}$ ; V. A. Nemiloff,  $1480^{\circ}$ ; R. Ruer and K. Kaneko,  $1491^{\circ}$ ; K. Friedrich,  $1494^{\circ}$ ; R. Sahmen, and W. A. Wahl,  $1493^{\circ}$ ; S. Umino,  $1489^{\circ}$ ; and A. G. C. Gwyer,  $1491^{\circ}$ . W. Guertler and M. Pirani gave  $1490^{\circ}$  for the best representative value; and L. I. Dana and P. D. Foote,  $1480^{\circ}$ . Other observations were made by F. Wever and U. Haschimoto, and G. Boeher. W. A. Lampadius made a determination on a very impure specimen. W. Guertler and G. Tammann observed that the presence of iron has very little influence on the m.p. of cobalt. R. C. Smith found that cobalt filings sintered at  $200^{\circ}$ , and precipitated cobalt at  $500^{\circ}$ . W. A. Wahl observed that molten cobalt is readily undercooled as much as  $216^{\circ}$  below its f.p., and solidification then occurs suddenly. At first molten cobalt readily attacks porcelain, but once the oxide has been removed, subsequent fusions do not cause any attacks. T. Carnelley discussed the relation between the m.p. and the coeff. of thermal expansion; W. Crossley, the relation between the m.p. and the at. vol.; G. A. Tomlinson, some interatomic relations of the m.p.; E. Kordes gave 2.65 for the change of entropy on melting; and W. Braunkbek, the effect of melting on the space-lattice.

As indicated previously, J. Pionchon observed an **allotropic transformation** at  $300^{\circ}$ ; and, according to I. I. Schukoff, there is a magnetic transformation or **transition point** at  $985^{\circ}$  whereby the magnetic metal becomes non-magnetic; W. Guertler and G. Tammann said that the transformation occurs at  $1150^{\circ}$ . For Lord Kelvin's (W. Thomson's) observation on the relation of the phenomenon to the law of transformation of energy, *vide* iron.

According to H. Moissan, cobalt is less volatile than nickel, so that under similar conditions in the electric-arc furnace, only 20 grms. of cobalt were distilled during the distillation of 50 grms. of nickel. O. Ruff and F. Keilig gave  $2415^{\circ}$  for the **boiling-point** of cobalt, or  $2375^{\circ}$  at 30 mm. press. W. R. Mott calculated  $2900^{\circ}$ . O. Ruff and co-workers found that the metal saturated with carbon begins to boil at  $2500^{\circ}$  and about 40 mm. press. R. W. Millar gave  $1885^{\circ}$  at 1 mm. press.,  $2635^{\circ}$  at 100 mm.,  $3050^{\circ}$  at 500, and  $3185^{\circ}$  at 760 mm.; and for the **vapour pressure** of the liquid,  $\log p = -1.865 \log T - 18610T^{-1} + 14.881$ . F. Wüst and co-workers<sup>9</sup> found the latent **heat of fusion** of cobalt to be 58.2 cal. per gram., or 3.44 Cals. per gram-atom at  $1478^{\circ}$ . J. W. Richards calculated 68 cal. per gram. S. Umino obtained 67.00 cal. per gram for the latent heat of fusion. E. Rabinowitsch and E. Thilo gave 0.15 volt for the heat of fusion; 3.94 volts for the heat of vaporization; and 4.09

volts for the heat of sublimation when 1 volt=23 Cals. The subject was studied by E. Kordes; and the relation between the heat of fusion and the vibration frequency, by W. Herz.

J. Thomsen<sup>10</sup> found the **heat of dissolution** in hydrochloric acid to be  $(\text{Co}, 2\text{HCl}, \text{aq.}) = 15.07$  Cals.; and in sulphuric acid,  $(\text{Co}, \text{H}_2\text{SO}_4, \text{aq.}) = 19.71$  Cals. According to W. G. Mixter, the **heat of oxidation** to amorphous cobaltous oxide is  $(\text{Co}, \frac{1}{2}\text{O}_2) = 50.5$  Cals., and to the crystalline oxide, 57.5 Cals.; whilst  $(3\text{Co}, 2\text{O}_2) = 193.4$  Cals. Z. Shibata and I. Mori gave  $(\text{Co}, \frac{1}{2}\text{O}_2) = 57,234$  cal. S. Umino found that the **heat of transformation** of cobalt from the hexagonal close-packed to the face-centred cubic lattice amounts to about 1.185 cal. per gram, or to  $1.16 \times 10^{-22}$  cal. for 1 molecule of cobalt. The magnetic transformation requires about 2.195 cal. per gram, or  $2.14 \times 10^{-22}$  cal. per molecule. E. D. Eastman, and G. N. Lewis and co-workers gave 7.2 cal. per degree at 25° for the **entropy** of cobalt. B. Bruzs, K. K. Kelley, W. Herz, R. D. Kleeman, and W. M. Latimer discussed this subject. R. von Dallwitz-Wegner discussed the **free energy**. Z. Shibata and I. Mori gave -51,612 cal. for the free energy of the reaction at 25.1°. H. Masumoto found a marked absorption of heat occurs at 427° on a rising temp., as  $\alpha$ -cobalt passes to  $\beta$ -cobalt, and an evolution of heat at 360° on a falling temp. S. Umino calculated from the sp. ht. curves of 98.135 per cent. cobalt, that the heat of transformation is 1.01 to 1.08 cal. per gram at 460°. Observations on the subject were made by J. Maydel; and U. Dehlinger discussed the changes of energy during the transformation.

For the colour of cobalt, *vide supra*. H. du Bois and H. Rubens<sup>11</sup> found the **index of refraction**,  $\mu$ , for electrolytic cobalt for light of wave-length,  $\lambda$ , to be :

$\lambda$	.	.	.	4310	4860	5393	6440	6700
$\mu$	.	.	.	2.10	2.39	2.76	3.10	3.22

The **absorption coefficient**, and the **reflecting power**,  $R$ , given by R. S. Minor, are :

$\lambda$	.	2313	2573	2749	2981	3467	3950	4500	5000	5500	5893
$k$	.	1.43	1.81	2.14	2.33	2.47	2.91	3.42	3.71	3.90	4.04
$\mu$	.	1.10	1.25	1.41	1.50	1.54	1.63	1.79	1.93	2.05	2.12
$R$	.	31.8	39.7	45.7	48.7	51.1	57.7	63.3	65.5	66.6	67.5

L. R. Ingersoll gave :

$\lambda$	.	7500	8700	1.00 $\mu$	1.25 $\mu$	1.50 $\mu$	1.75 $\mu$	2.00 $\mu$	2.25 $\mu$
$k$	.	4.85	5.37	5.73	6.30	6.73	6.81	6.95	7.18
$\mu$	.	2.71	3.18	3.63	4.50	5.22	5.53	5.63	5.65
$R$	.	71.0	72.5	73.3	74.3	75.1	75.1	75.7	76.5

Observations were also made by A. Q. Tool, C. Zakrzewsky, I. C. Gardner, A. Kundt, A. Pflüger, G. Quincke, W. Voigt, and D. Shea. C. A. Skinner and A. Q. Tool discussed the optical properties of thin films of cobalt; and H. Behrens, the double refraction of films obtained by spluttering. W. W. Coblentz gave for the reflecting power :

$\lambda$	.	1.06 $\mu$	1.71 $\mu$	3.06 $\mu$	3.96 $\mu$	5.24 $\mu$	6.75 $\mu$	8.02 $\mu$	9.38 $\mu$	10.49 $\mu$	12.03 $\mu$
$R$	.	67.5	71.5	76.7	80.7	86.2	92.7	95.8	96.4	96.8	96.6

and observations were also made by W. W. Coblentz and R. Stair, E. O. Hulbert, A. Q. Tool, R. S. Minor, P. Drude, L. R. Ingersoll, A. Hunke, A. Heydweiller, A. Bromer, and K. Fajans and H. Kohner. H. Geisler studied the anomalous dispersion; and A. Kundt, the absorption of light by thin films.

H. Knoblauch found the **polarization angle** for ultra-red heat rays to be 79.00; and 72.50 for yellow-light. E. Hirsch studied the circular polarization. J. H. Gladstone gave 10.4 for the **refraction equivalent**, and 0.177 for the sp. **refractive power**. W. J. Pope gave 13.18 for the refraction equivalent of cobalt; and the scattering of light by cobalt-blue was studied by G. I. Pokrowsky.

C. L. Utterback<sup>12</sup> measured the total **radiation energy**,  $E$ , of cobalt at  $T^\circ \text{K.}$ , and found that  $E=c_1T^{5.20}$  for temp. between  $672^\circ \text{K.}$  and  $1320^\circ \text{K.}$ ; and  $E=c_2T^{4.62}$ , between  $1380^\circ \text{K.}$  and  $1590^\circ \text{K.}$  There is a rapid change in the emission near the transformation point,  $1348^\circ \text{K.}$ , at which temp. there are changes in the susceptibility, permeability, resistance, sp. ht., and thermal expansion. G. K. Burgess and R. G. Waltenburg found that with light of wave-length  $0.65\mu$ , the emissive power,  $E$ , for cobalt near its m.p. is 0.36 for the solid, and 0.37 for the liquid. G. R. Green-slade determined the effect of temp. on the emission of energy.

The **Kerr effect** was studied by E. van Aubel,<sup>13</sup> H. Behrens, H. du Bois, W. Dziewulsky, P. D. Foote, E. H. Hall, L. R. Ingersoll, A. Kundt, J. G. Leatham, P. Martin, C. A. Skinner and A. Q. Tool, C. Snow, and W. Voigt; and the rotation of the plane of polarization by passage through thin layers of cobalt in a magnetic field, the so-called **Faraday effect**, by H. Behrens, H. du Bois, C. J. Gorter, E. Hirsch, A. Kundt, W. Lobach, E. Miescher, C. A. Skinner and A. Q. Tool, and W. Voigt.

Cobalt gives no distinctive coloration to the colourless flame; but the **flame spectrum** of cobalt has been examined by A. Gouy,<sup>14</sup> J. N. Lockyer, E. Diacon, L. de Boisbaudran, W. N. Hartley, W. N. Hartley and H. Ramage, C. de Watteville, A. Hagenbach and H. Konen, J. M. Eder and E. Valenta, G. D. Liveing and J. Dewar, J. Meunier, H. Auerbach, A. Harnack, and E. N. da C. Andrade. A. K. Russanoff studied the acetylene flame spectrum of nickel. The **spark spectrum** shows a number of lines and, according to J. Formanek, the more important of which are 5641 in the yellowish-green; 5483— $\epsilon$ , Fig. 6—5353 and 5340— $\alpha$ , Fig. 6—5280, 5267— $\beta$ , Fig. 6—5212— $\delta$ , Fig. 6—and 5154 in the green; 4868— $\gamma$ , Fig. 6—4840— $\zeta$ , Fig. 6—4815 and 4793 in the blue; 4533 in the indigo;

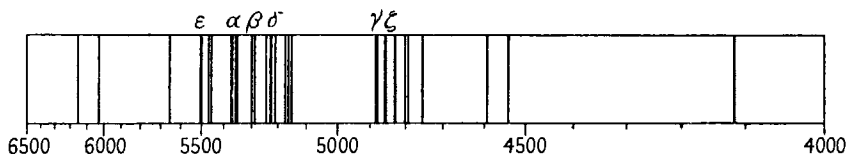


FIG. 6.—The Spark Spectrum of Cobalt.

and 4119 in the violet. The green double lines,  $\alpha$  and  $\beta$ , are characteristic, and so also are the blue lines,  $\gamma$  and  $\zeta$ , and the green line,  $\epsilon$ . The spark spectrum was examined by W. E. Adeney, L. and E. Bloch, L. de Boisbaudran, R. Capron, G. C. Ciamician, E. Demarcay, J. M. Eder, J. M. Eder and E. Valenta, F. Exner and E. Hatschek, J. H. Findlay, H. Finger, A. Hagenbach and H. Konen, W. N. Hartley, W. Huggins, E. O. Hulburt, G. Kirchhoff, W. Kraemer, G. D. Liveing and J. Dewar, J. N. Lockyer, O. Lohse, F. McClean, W. A. Miller, J. Parry and A. E. Tucker, J. H. Pollok, J. H. Pollok and A. G. G. Leonard, T. R. Robinson, S. P. de Rubies, T. Takamine and S. Nitta, and R. Thalén. W. F. Meggers, W. F. Meggers and F. M. Walters, and E. O. Hulburt studied the spark spectrum under water.

The **arc spectrum** was studied by Lord Blythwood and W. A. Scoble, K. Burns, A. Cornu, F. Dhein, F. Exner and E. Hatschek, J. H. Findlay, C. E. Greider, S. Hamm, B. Hasselberg, C. Horner, J. Janssen, A. Krebs, G. D. Liveing and J. Dewar, J. N. Lockyer, J. C. McLennan and co-workers, H. M. Randall and E. F. Barker, H. A. Rowland, S. P. de Rubies, H. Slevogl, L. Stütting, T. Takamine and S. Nitta, W. Vahle, and F. M. Walters. The spectrum in the discharge tube with a glowing cathode resembles the arc spectrum; and it was examined by M. Kimura and G. Nakamura, J. H. Pollok, C. Wali-Mohammad, and L. Janicki.

The **absorption spectrum** of the vapour of cobalt was examined by J. N. Lockyer and W. C. Roberts-Austen, and W. F. Meggers and co-workers; the spectrum of gaseous explosions, by G. D. Liveing and J. Dewar; and the spectrum of cobalt in the electric furnace, by F. Dhein, G. A. Hemsalech, and A. S. King. The **ultra-**

**violet spectrum** was examined by V. Schumann, J. M. Eder, F. Exner and E. Hatschek, R. J. Lang, J. H. Findlay, E. Bayle and L. Amy, R. Volterra, L. and E. Bloch, T. Takamine and S. Nitta, J. C. McLennan and co-workers, R. G. zu Dohna, and H. Becquerel; and the **ultra-red spectrum**, by W. F. Meggers and C. C. Kiess, Lord Blythwood and W. A. Scoble, L. Stütting, and H. M. Randall and E. F. Barker. The effect of *pressure* on the spectral lines of iron was studied by W. J. Humphreys, C. D. Liveing and J. Dewar, W. B. Anderson, H. Finger, and H. Konen and H. Finger; the effect of *temperature*, by H. Auerbach, and W. N. Hartley; the *intensity* of the lines by W. Clarkson, P. W. Merrill, G. Nakamura, L. S. Orstein and co-workers, and L. S. Orstein and T. Bouma; the explosion spectrum, by H. Nagaoka and co-workers; the effect of the *oscillating discharge*, by G. A. Hemsalech; the effect of the *self-induction*, by G. A. Hemsalech, and P. B. Huber; the *anomalous dispersion*, by H. Geisler; the *enhanced lines*, by M. Kimura and G. Nakamura, and J. N. Lockyer; the effect of the *medium*, by H. Finger, P. B. Huber, W. B. Anderson, T. R. Robinson, G. A. Hemsalech, A. Schuster and G. A. Hemsalech, and H. Konen and H. Finger; the effect of a *magnetic field*—the **Zeeman effect**—by J. M. Graftdyk, S. Rybar, G. J. Elias, C. Wali-Mohammad, P. A. van der Harst, J. Kunz, F. M. Walters, J. H. Findlay, and J. H. van Vleck and A. Frank; *current strength*, etc., by M. Kimura and G. Nakamura; *reversed spectra*, W. F. Meggers, and A. Cornu; the *energy* of arc and spark spectra, by A. Pflüger; and the effect of an *electric field*—the **Stark effect**—by J. A. Anderson, M. Kimura and G. Nakamura, T. Takamine, and H. Nagaoka and Y. Sugiura. The *ultimate rays* were discussed by A. de Gramont, L. S. Orstein and T. Bouma, W. R. Mott, J. Bardet, F. Löwe, L. de Boisbaudran, H. N. Russell, E. Bayle and L. Amy, T. Negresco, M. Catalan and K. Bechert, W. F. Meggers and C. C. Kiess, and W. N. Hartley and H. W. Moss. The qualitative analysis of mixtures with cobalt was discussed by J. Parry and A. E. Tucker, A. Schleicher, and W. Gerlach and K. Ruthardt; and the quantitative analysis, by F. Twyman and C. S. Hitchin. The *structure and regularities of the line spectrum* of cobalt was studied by E. von Angerer and G. Joos, K. Bechert, C. G. Bedreag, M. C. W. Buffam and H. J. C. Ireton, B. Cabrera, W. M. Cady, M. A. Catalan, M. A. Catalan and K. Bechert, G. Ciamician, C. R. Davidson and F. J. M. Stratton, J. H. Findlay, R. C. Gibbs and H. E. White, S. Goudsmit, A. de Gramont, W. N. Hartley, F. Hund, L. Janicki, C. C. Kiess and O. Laporte, M. Kimura and G. Nakamura, O. Laporte, O. Laporte and W. F. Meggers, O. Laporte and A. Sommerfeld, W. F. Meggers, W. F. Meggers and C. C. Kiess, W. F. Meggers and F. M. Walters, R. A. Merrill, K. R. More, F. P. Mulder, A. A. Noyes and A. O. Beckman, P. G. Nutting, L. S. Orstein and T. Bouma, E. Paulson, R. Rudy, S. Rybar, H. N. Russell, M. N. Saha and B. B. Ray, M. Sawada, A. W. Smith and M. Muskat, C. P. Snow and F. I. G. Rawlins, L. A. Sommer, N. K. Sur, N. K. Sur and K. Majumder, I. Tamm, C. Wali-Mohammad, and F. M. Walters. No **series spectra** have been detected. A. T. Williams discussed the relation between valency and multiple spectra.

Red, aq. soln. of cobalt chloride become violet at 100°. The phenomenon was studied by J. Bersch,<sup>15</sup> and J. Kallir. With conc. hydrochloric or sulphuric acid, the colour of the soln. becomes blue, and this the more readily, the higher is the temp. The red crystals of the hexahydrate,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , when heated, lose water, forming a lower hydrate, and the colour changes to violet-red, or bluish-violet. The anhydrous salt is pale blue. Aq. soln. of cobalt chloride can be red, violet, or blue. The colour depends on the temp. and conc. Red, aq. soln. become blue when mixed with the metal chlorides. The chlorides of calcium and magnesium are specially active, so that, even at ordinary temp., they change the colour to violet or blue. Hydrochloric acid and sodium chloride are not so active, but they enable the blue colour to appear at a lower temp. than is the case with soln. of cobalt chloride alone. The chlorides of zinc, mercury, antimony, tin, etc., act in the converse way and favour the change of colour from blue or violet back to the original red. Conc. soln. in methyl or ethyl alcohol are blue.

According to J. Formanek, the **absorption spectrum** of aq. rose-coloured soln. of cobalt chloride or nitrate, suitably diluted, has a strong, green band at 5160—Fig. 7; and two very weak bands at 4795 and 4610, which are not visible in dil.

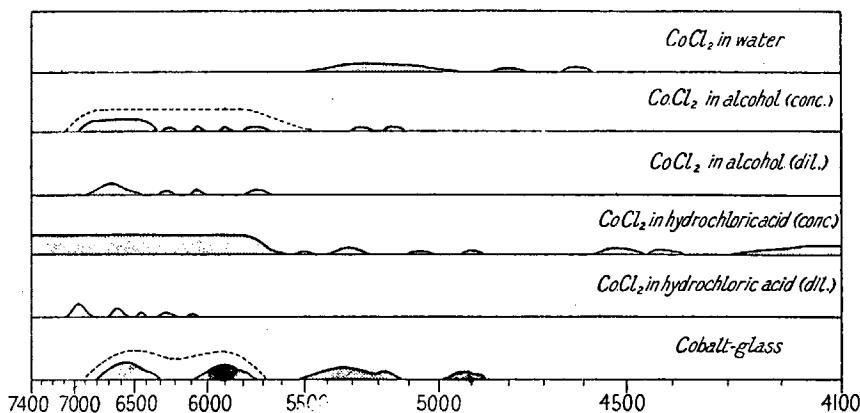


FIG. 7.—The Absorption Spectra of Cobalt Salt Solutions.

soln. Defining the mol. extinction coeff.,  $A$ , by the equation  $I = I_0 10^{-Ad}$ , where  $I_0$  denotes the original intensity of the light, and  $I$  the final intensity after passing through  $d$  cm. of soln. containing  $C$  mols. of salt per litre, R. S. Houstoun and co-workers found that the mol. extinction coeff.,  $A$ , is a function of the wave-

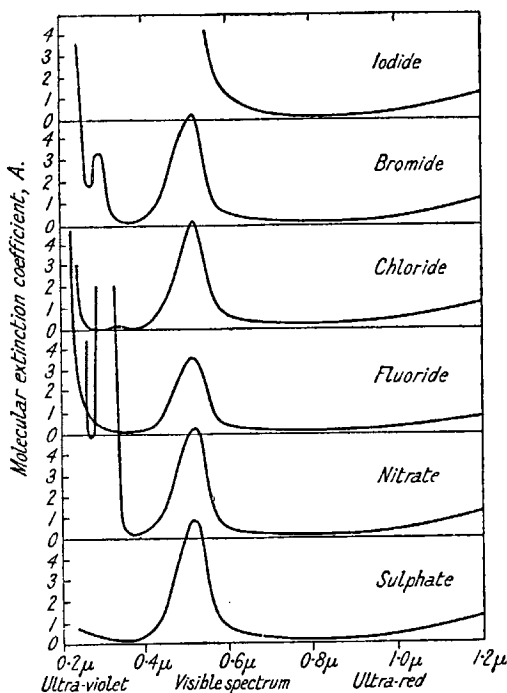


FIG. 8.—The Absorption Spectra of Aqueous Solution of Cobalt Salts.

sorption at the red-end of the spectrum with a rise of temp. is clearly shown by sat. soln. of cobalt chloride either alone or admixed with calcium chloride. The

length,  $\lambda$ , as indicated for soln. of different cobalt salts, in Fig. 8. The value of the coeff.,  $A$ , varies with the concentration,  $C$ , of the soln.; and also with the temp. The results with the chloride for cold, dil. soln., cold, conc. soln. and hot, conc. soln. are illustrated by Fig. 9. W. J. Russell observed a great similarity in the absorption spectra of fused mixtures of cobalt and chloride and alkali chlorides, of blue soln. of cobalt chloride in hydrochloric acid, of conc. soln. of cobalt chloride in methyl, ethyl, and amyl alcohols, glycerol, and various esters. The results were in all cases ascribed to the presence of free, anhydrous cobaltous chloride. The spectra of aq. soln. varied with the concentration; saturated soln. gave a spectrum with bands at  $\lambda=610$  and  $625$  characteristic of the anhydrous chloride, whilst dil. soln. gave a band between  $\lambda=550$  and  $485$ , and this was ascribed to the hydrated chloride. W. N. Hartley found that the increase in ab-

general results show that soln. of cobaltous chloride in hydrochloric acid and in sat. soln. of calcium chloride contain something which is also produced in conc. aq. soln. with a rise of temp. The question arises: what is this something?

Several attempts have been made to explain the colour phenomena of the cobalt salts. The simple hydration theory was discussed by A. Étard, R. A. Houston and co-workers, A. Benrath, C. H. L. von Babo, H. Schiff, J. H. Gladstone, C. R. C. Tichborne, W. J. Russell, W. J. Russell and W. J. Orsman, A. Potilitzin, G. N. Wyruboff, G. Charpy, M. S. Wreusky, and W. N. Hartley; the molecular compound theory, by R. Engel, G. N. Wyruboff, H. le Chatelier, A. Chassevant, and F. Schlegel; the allotropic theory, by J. Bersch; the ionization theory, by W. Ostwald, W. C. D. Whetham, R. Salvadori, and N. Tarugi and G. Bombardini; the complex ion theory, by F. G. Donnan and H. Bassett, H. Bassett and H. H. Croucher, G. Rudorff, and H. G. Denham; and the hydrated ion theory, by P. Vaillant, G. N. Lewis, C. Mazzetti, H. C. Jones and co-workers, and A. Kotschubei. This subject is discussed in connection with the colour of cobaltous chloride. J. Piccard and E. Thomas studied the colour of cobalt ions; H. J. Witteveen and E. F. Farnau, the colours produced by the cobalt oxides.

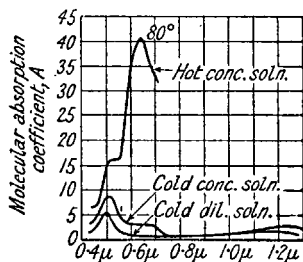


FIG. 9.—The Effect of Temperature and Concentration on the Absorption Spectrum of Cobalt Chloride Solutions.

H. C. Jones and co-workers also examined the absorption spectra of cobalt salts, and tried to show that the gradual shift of an absorption band, as one salt is transformed into another by replacement of the acid radical, indicates that intermediate compounds are formed; but T. R. Merton showed that the alleged shift is only apparent, and is a consequence of the method of measurement employed in the work. T. Bayley discussed the relations of the absorption spectra salts of the iron family of elements. The absorption spectra of soln. were also observed by J. Angerstein, D. Brewster, W. Boehlendorff, J. Conroy, J. M. Hiebendaal, J. Dreisch, C. Kubierschky, G. B. Rizzo, C. P. Smyth, J. Landauer, M. Kahanowicz and P. Orecchioni, W. R. Brode, R. Samuel and co-workers, S. Hakomori, R. J. Macwalter and S. Barratt, B. E. Moore, W. N. Hartley, C. H. Wolff, S. Kato, A. Étard, A. Rosenheim and V. J. Meyer, T. Bayley, J. Moir, W. J. Russell, etc. The use of the absorption spectra for the qualitative analysis of members of the iron family of elements was discussed by H. W. Vogel, and J. Formanek; and the effect of press., by F. G. Wick.

According to J. Formanek, the soln. of cobalt chloride in absolute alcohol is sky-blue, and with conc. soln., the spectra have a broad absorption band extending into the red and yellow, and there are feeble bands at 5265 and 5150. By diluting the soln. with absolute alcohol, the feeble bands at 5265 and 5150 disappear, and the strong band in the red breaks up into small, feeble bands, 6245, 6063, 5906, 5720, and a strong band at 6648—*vide* Fig. 10. With very dil. soln., there are only the

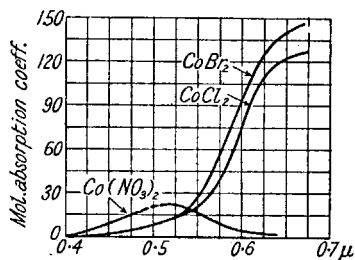


FIG. 10.—The Absorption Spectra of Alcoholic Solutions of Cobalt Salts.

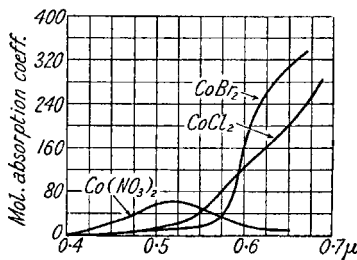


FIG. 11.—The Absorption Spectra of Acetone Solutions of Cobalt Salts.

strong band 6648, and the weak bands 6245 and 6063. The alcoholic soln. of cobalt nitrate is reddish-violet, and like the aq. soln. of cobalt nitrate, it has a strong, broad



band about  $5240$ , and in conc. soln. only, feeble bands at  $4830$  and  $4620$ . R. A. Houstoun and co-workers' results for soln. of cobalt salts in alcohol and in acetone are summarized in Figs. 10 and 11. The absorption is greater in these soln., and the results are more characteristic of the molecule than is the case with

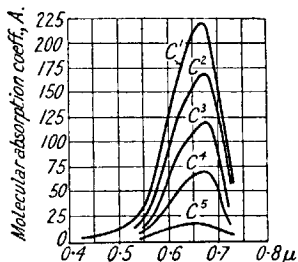


FIG. 12.—The Effect of Water on Alcoholic Solutions of Cobalt Chloride.

aq. soln. The absorption in alcohol and acetone varies very greatly from one salt to another, and they said that "it seems to depend more on the bonds connecting the base to the acid radical." There is evidence of a chemical change between acetone and cobalt bromide. When water is gradually added to an alcoholic soln. of cobalt chloride, the colour gradually changes until it reaches the colour of an ordinary aq. soln. In pure alcoholic soln. there is a very pronounced maximum at  $675\mu$ : as water is added to the extent of one-twentieth of its value in the purely alcoholic soln. where there were present  $C_1^1=1.028$  mols of cobalt chloride per litre, and no water  $C_{23}^1=0$ . For the successive solns.  $C_1^2=0.9766$  and  $C_2^2=3.3$ ;  $C_1^3=0.9252$  and  $C_2^3=5.75$ ;  $C_1^4=0.8738$  and  $C_2^4=9.35$ ; and  $C_1^5=0.8224$  and  $C_2^5=12.22$ ; etc. The results, Fig. 12, show that the maximum height of the band decreases approximately in the same ratio, and there is a slight displacement towards the red. For  $C_1^7=0.514$  and  $C_2^7=29.51$  there is no trace of this band, and the results are the same as with dil. aq. soln.

The cobalt chloride thus exists in two phases: one characterized by a band in the red (blue phase), and as water is added this passes into a phase characterized by a band in the green at  $510\mu$  (red phase). Since the maximum with the green band in aq. soln. not approaching saturation is about 6, and the maximum with the red band is about 232, the band in the green is observed by the side of the other band if more than one-tenth of the salt is in the blue phase. After applying the law of mass action to the results, it was concluded that in the red phase each cobalt chloride molecule is associated with approximately 15 mols. of water to form a polyhydrate. The absorption bands of cobalt chloride thus correspond with the anhydrous molecule ( $680\mu$ ), the hexahydrate ( $550\mu$  and  $490\mu$ ), and the polyhydrate. W. Hardt also studied the spectra of alcoholic soln.

J. Formanek found that cobalt chloride forms a blue soln. with hydrochloric acid, and this gives a characteristic absorption spectrum, Fig. 13. A conc. soln.

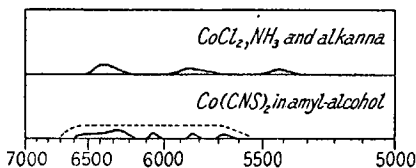


FIG. 13.—Absorption Spectra of Cobalt Salts.

has bands at  $5495$ ,  $5294$ ,  $5041$ ,  $4885$ ,  $4510$ , and  $4418$ , besides a strong, broad band in the red, and one in the violet. The bands at  $5041$  and  $4885$  are scarcely visible; and those at  $4510$  and  $4418$  are inclined to merge into one another. With dil. soln., the narrow bands, observed with the conc. soln., disappear, and the broad band in the red breaks up into bands at  $6933$ ,  $6600$ ,  $6415$  (weak),  $6236$ , and  $6090$ . A

very small proportion of cobalt chloride in conc. hydrochloric acid shows the absorption bands very clearly. W. R. Brode, and W. R. Brode and R. A. Morton showed that the principal absorption band of soln. of cobalt chloride in conc. hydrochloric acid consists of six superimposed component bands. The frequencies of the maximum of these bands and also of the bands in the blue and green regions are integral multiples of  $12.28$ . A soln. of cobalt bromide in hydrobromic acid shows similar bands, but with fundamental frequencies of  $11.70$ . A soln. of cobalt iodide in hydriodic acid also shows absorption bands, the frequencies of maximum absorption being integral multiples of a fundamental frequency of  $10.79$ .

When a neutral soln. of cobalt chloride is mixed with tincture of alkanna, a

violet soln. is produced, and besides the absorption spectrum of alkanna, it shows a feeble band at 6320. If ammonia be added, a new absorption spectrum appears with three bands: 6370, 5845, and 5405, Fig. 13. A small excess of ammonia may give a blue precipitate. With a soln. of cobalt nitrate, and tincture of alkanna, there is a weak band at 6290; and after the addition of ammonia, the band is displaced more to the right than is the case with cobalt chloride, and there are bands at 6354, 5832, and 5395.

A. N. Nikolopoulos, and R. Luther and A. N. Nikolopoulos showed that the absorption spectrum of the cobaltamines is dependent only on the composition of the complex. The replacement of  $\text{NH}_3$  by  $\text{NO}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{Cl}$ , and  $\text{Br}$  in the complex causes a displacement of the absorption towards the red end of the spectrum; and the replacement of  $\text{NH}_3$  by  $\text{NO}_2$  produces a displacement towards the violet end. In accord with the electronic theory, the stability of analogous compounds is greater the further the absorption bands extend towards the violet, and the photochemical sensitiveness is greater, the steeper is the absorption curve. Y. Shibata and G. Urbain also found that, with the exception of the  $\text{NO}_2$ -group, the negative radicals provoke a displacement of the less refrangible bands towards the red. The absorption spectra of the cobaltamines have two bands with minima near 2000 and 3000, and these are characteristic of the tervalent cobalt atom acting as a chromophore. Observations were also made by C. Schleicher, R. Samuel and co-workers, E. Valla, K. Matsuno, A. Uspensky and co-workers, F. W. Beyer, J. Lifschitz and E. Rosenbohm, J. Kranig, A. Gordienko, and J. Angerstein.

When a soln. of a cobalt salt is treated with ammonium thiocyanate, the liquid becomes dark red; and if amyl alcohol is added, the cobalt thiocyanate colours the alcoholic layer greenish-blue. The absorption spectrum of the conc. amyl alcoholic soln. has an intense, orange-yellow band; and on dilution the band breaks up into four others at 6258, 6044, 5807, and 5636—Fig. 13. If the soln. be still further diluted, the bands at 5807 and 5635 disappear. The presence of nickel, chromium, manganese, and zinc do not interfere with these reactions as a qualitative test for cobalt. The acetone soln. are similarly used as a qualitative test for cobalt.

According to J. Conroy, J. Formanek, and J. Moir, blue cobalt-glass, not too dark, furnishes an absorption spectrum, Fig. 13, with a broad, intense band extending into the red and yellow, and there is a broad, weak band at 5348, and one which is just perceptible at 4934. If a paler cobalt-glass be used, in place of the broad band in the red and yellow, there are two bands, 6560 and 5900, whilst the band at 5348 becomes weaker, and that at 4934 is no longer visible. This absorption spectrum is characteristic of cobalt-glass, and enables it to be distinguished from blue copper-glass; and it also enables artificial cobalt-blue sapphires to be distinguished from natural sapphires. W. Abney and E. R. Festing observed a band at  $1.32\mu$  in the ultra-red spectrum of cobalt-glass. Observations were also made by M. Luckeish, D. Starkie and W. E. S. Turner, S. Sugie, T. Dreisch, W. R. Brode, and J. W. Mellor.

H. Kulenkampf,<sup>16</sup> and W. Duane and T. Shimizu studied the continuous **X-ray spectrum**. The K-series of the X-ray spectrum includes the lines  $\alpha, \alpha=1.785287$ ;  $\alpha_2\alpha'=1.789187$ ;  $\alpha_3\alpha_4=1.7774$ ;  $\beta, \beta=1.617436$ ;  $\beta_2\gamma=1.60562$ ; and  $\beta'=1.62011$ . Observations were reported by S. K. Allison, A. H. Barnes, H. Beuthe, F. de Boer, D. K. Berkeley, D. M. Bose, D. Coster and M. F. Druyvesteyn, G. B. Deodhar, V. Dolejssek, V. Dolejssek and H. Filcakova, W. Duane and co-workers, S. Erikson, P. Günther and co-workers, E. Hjalmar, S. Idei, S. Kawata, B. Kievit and G. A. Lindsay, H. G. J. Moseley, B. C. Mukherjee and B. B. Ray, G. Ortner, S. Pastorello, M. Privault, B. B. Ray, O. W. Richardson and co-workers, M. N. Saha and B. B. Ray, N. Seljakoff and co-workers, N. Siegbahn and co-workers, N. Stenstrom, R. Thoraues, J. Valasek, B. Walter, J. H. Williams, G. Wentzel, and S. Yoshida. The K-absorption limits observed by F. de Boer are for the metal, 1.6042 Å., for bivalent compounds, 1.6029 Å., and for ter-

valent compounds, 1.6022 Å. Observations were also made by S. Björck, N. Bohr and D. Coster, R. Brdica, V. Dolejšek and K. Pestrecoff, W. Duane and K. F. Hu, B. Kievit and G. A. Lindsay, B. C. Mukherjee and B. B. Ray, M. Siegbahn, E. C. Stoner, R. Thoraues, and B. Walter. The structure of the K-lines was examined by H. Lang, F. de Boer, B. Kievit and G. A. Lindsay, B. C. Mukherjee and B. B. Ray, B. B. Ray, and B. B. Ray and P. C. Mahanti. The L-series of X-ray spectrum included  $\alpha, \alpha-\alpha_2\alpha'=15.94$ ;  $\beta, \beta=15.62$ ;  $\epsilon=18.20$ ; and  $\eta\eta=17.77$ . They were studied by S. Björck, N. Bohr and D. Coster, V. Dolejšek and K. Pestrecoff, H. Hirata, C. E. Howe, G. Kellström, H. Lang, B. C. Mukherjee and B. B. Ray, F. P. Mulder, M. Siegbahn and R. Thoraues, E. C. Stoner, C. H. Thomas, R. B. Witmer and J. M. Cook, S. Björck, W. Stenström, R. Thoraues, J. H. van der Tuuk, and B. Walter. The M-series were investigated by U. Andrewes and co-workers, S. Björck, N. Bohr and D. Coster, K. T. Compton and C. H. Thomas, M. Levi, B. C. Mukherjee and B. B. Ray, O. W. Richardson and co-workers, B. B. Ray and R. C. Mazumdar, E. C. Stoner, C. H. Thomas, and B. Walter; and the N-series by F. P. Mulder, and B. Walter. M. A. Valouch, and J. Palacios and M. Velasco studied the structure of the X-ray spectrum.

C. G. Barkla and C. A. Sadler<sup>17</sup> studied the penetrating power or hardness of the **X-rays**, and in general it is greater, the greater is the degree of exhaustion of the tube, but for a given tube, it depends solely on the potential difference of the electrodes. The penetrability is generally proportional to the 5th power of the at. wt. of the radiator. If  $I_0$  be the intensity of a parallel beam of homogeneous X-rays, incident normally on a plate of absorbing material, then, the intensity  $I$  at a depth  $x$  is  $I=I_0e^{-\lambda x}$ . The values of the coeff.  $\lambda$  divided by the density,  $D$ , for different absorbers, when radiator is cobalt, are, for K-radiations:

	C	Mg	Al	Fe	Ni	Cu	Zn	Ag	Sn	Pt	Au
$\lambda/D$	7.96	63.5	71.6	67.2	67.2	75.3	91.5	314	392	281	306

Observations on the **absorption** of X-rays were also made by O. W. Richardson and F. S. Robertson, F. K. Richtmyer and F. W. Warburton, J. Veldkamp, C. G. Barkla, C. G. Barkla and V. Collier, H. T. Meyer, H. Richardson, E. Rupp, C. A. Sadler and A. J. Steven, L. H. Martin and K. C. Lang, O. Stelling, K. Grosskurth, and M. Siegbahn. The absorption coeff.  $\lambda$ , for K-radiation in gases under normal conditions, were measured by C. G. Barkla and V. Collier, and E. A. Owen:

	Air	H <sub>2</sub> S	SO <sub>2</sub>	C <sub>2</sub> H <sub>5</sub> Br
$\lambda$	0.0165	0.181	0.20	0.407

Observations were also made by L. M. Alexander, T. E. Aurén, G. B. Bandopadhyaya, L. Benoist, W. L. Bragg and H. L. Porter, W. L. Bragg and J. West, H. Kulenkampff, A. Hébert and G. Reynaud, M. Ishino and S. Kawata, R. Ledoux-Lebard and A. Dauvillier, E. A. Owen, J. A. Prins, H. S. Read, F. K. Richtmyer and F. W. Warburton, M. Siegbahn, and K. A. Wingardh. The **scattering** of the X-rays was studied by R. W. Jones and G. W. Brindley, E. A. Owen, F. K. Richtmyer and F. W. Warburton, and K. A. Wingardh; the **reflection** of the X-rays, by J. A. Prins, E. Rupp, D. K. Berkey, and H. T. Meyer; the X-ray **fluorescence**, by C. G. Barkla, L. H. Martin, and W. Kossel; the secondary and tertiary X-rays, by C. G. Barkla; the production of X-rays, by C. S. Brainin, O. W. Richardson, and O. W. Richardson and F. S. Robertson; the production of X-rays by the  $\alpha$ -rays of radium-A, and radium-C, by H. Richardson; long range particles, by G. Kirsch and H. Pettersson; and the effect of oxidation on the emission of X-rays by cobalt, by L. P. Davies.

The **vibration frequency**—*vide* 1. 13, 19—of cobalt has been calculated from various formulæ. C. Benedicks<sup>18</sup> thus obtained values ranging from  $7.7 \times 10^{12}$  to  $9.1 \times 10^{12}$ ; C. E. Blom,  $8.3 \times 10^{12}$ ; A. F. Scott,  $8.3 \times 10^{12}$ ; H. S. Allen,  $8.87 \times 10^{12}$ ; W. Biltz,  $6.2 \times 10^{12}$ ; W. Herz,  $8.12 \times 10^{12}$ ; and F. Simon and M. Ruhemann,  $1.26 \times 10^{12}$  to  $8.0 \times 10^{12}$ . Calculations were also made from the entropy by S. Pagliani, and W. Herz; from the at. wt. and mol. vol., by A. Stein;

and from the hardness, cohesion, and thermal expansion, by C. Benedicks. K. F. Slotte studied the velocity of the molecules at 0°.

H. B. Wehlin<sup>19</sup> observed that when cobalt is heated to a temp. where vaporization is appreciable, ions with a single charge are emitted, but no ions with a double charge were observed. M. N. Davis, L. P. Davies, and G. B. Welch studied the **photoelectric effect** of cobalt, and G. B. Welch gave 1365 Å. for the photoelectric threshold of cobalt; J. J. Weigle, T. Pavolini, L. P. Davies, U. Nakaya, and W. Frese studied the effect of occluded gases on the photoelectric effect. H. S. Allen, and W. Frese noted that oxidizing agents which make the metal passive also reduce the photoelectric sensitiveness. A. B. Cardwell found that as the temp. of a cobalt wire, in vacuo, is gradually raised, the sensitiveness for a photoelectric current is greater with undercooled, face-centred cubic cobalt than it is with ordinary close-packed, hexagonal cobalt. At a higher temp., the two curves coincide; and with a falling temp., the curve tends to a maximum which is not attained on the curve for a rising temp. The maximum thermionic current is about  $\frac{1}{15}$ th as strong as the maximum photoelectric current; and it is probable that the thermionic work function is less for cubic than it is for hexagonal cobalt. The long-wave limit for the photoelectric emission of cobalt, having a face-centred cubic lattice, is between 2967 Å. and 3022 Å., and for cobalt with a close-packed hexagonal lattice, between 2757 Å. and 2967 Å. J. J. Weigle gave 3450 Å. O. Berg and P. Ellinger, G. L. Locher, T. Pavolini, and G. B. Welch studied the photoelectric emission of electrons from compressed metal.

A. Günther-Schulze studied the work of electron emission; E. Rupp, and F. Butavand, the absorption of electrons; M. N. Davis, F. Simon, K. Hayakawa, L. P. Davis, U. Nakaya, and W. Espe. the emission of electrons; A. Gehrts, and M. N. Davis, the reflection of electrons; and C. J. Davisson and L. H. Germer, the diffraction of electrons. W. J. Russell discussed the feeble action of cobalt on photographic plates in the dark; W. Merckens, the formation of hydrogen dioxide by silver bromide gelatine; artificial radioactivity, by E. Fermi and co-workers; and N. Piltschikoff, the emission of the so-called Moser rays capable of passing through paper, celluloid, gelatine, and aluminium, and of decomposing silver bromide. R. Robl observed no luminescence in ultra-violet light; and R. E. Nyswander and B. E. Cohn studied the effect of cobalt on the thermoluminescence of glass.

B. B. Ray and R. C. Mazumdar,<sup>20</sup> A. A. Noyes and A. O. Beckmann, and J. H. Findlay investigated the critical potentials of soft X-rays. H. N. Russell gave for the series and ionization potentials for singly-charged atoms, respectively, 7.81 and 17.2 volts; for neutral atoms, 8.25, 9.03, 7.32, and 6.92 volts; and for ionized atoms, 16.62, 15.84, and 17.04 volts. For the ionization potential of neutral atoms, R. N. Ghosh gave 8.52 volts; N. K. Sur, 8.51 volts; L. A. Sommer, 8.4 volts; H. N. Russell, L. Rolla and C. Piccardi, 7.81 volts; and M. A. Catalan, 7.8 volts. A. C. Davies and F. Horton, E. H. Hall, C. H. Thomas, and U. Andrewes and co-workers obtained a series of values for the critical voltages of cobalt; and O. W. Richardson and co-workers found that a sequence of these can be represented by  $V=179.5-2357n^{-2}$  volts, where  $n=4, 5, 6, 7, 8, 10$ , and 12.

H. E. Watson and G. R. Paranjpe,<sup>21</sup> and G. R. Paranjpe found that under comparable conditions the cathode fall of potential in neon is 150 volts; in helium, 161 volts; in argon, 184 volts; and in nitrogen, 259 volts. The results in hydrogen were irregular. A. Schaufelberger observed that the normal fall of potential in air thoroughly dried is 381 volts. A. Günther-Schulze, K. Meyer and A. Günther-Schulze, F. Schröter, V. Kohlschütter, and H. P. Walmsley studied the cathodic spluttering of cobalt—*vide supra*, colloidal cobalt. C. E. Guye and L. Zebrikow, H. Nagaoka and Y. Sugiura, and W. G. Cady studied the difference of potential in the electric arc between cobalt electrodes. M. Haitinger measured the intensity of the ultra-violet ray from the cobalt arc-light.

The **electrical resistance** of cobalt, measured by H. Copaux,<sup>22</sup> is  $5.5 \times 10^{-6}$  ohm per cm. cube at  $0^\circ$ ; R. Ruer and K. Kaneko gave  $6.4 \times 10^{-6}$  ohm per cm. cube at room temp. for purified cobalt previously heated to  $1150^\circ$  and slowly cooled; C. G. Knott,  $11.2 \times 10^{-6}$  ohm per cm. cube at  $100^\circ$ , and  $15.9 \times 10^{-6}$  ohm at  $200^\circ$ ; whilst G. Reichardt found for 99.8 per cent. cobalt at  $20^\circ$ ,  $R = 9.73 \times 10^{-6}$  ohm per cm. cube, when heated to  $160^\circ$ , and  $R = 9.94 \times 10^{-6}$  when not so heated. A. Schulze found for the sp. resistance of three samples with 99.2 per cent. of cobalt at  $20^\circ$ ,  $R = 0.056363$ ,  $0.056480$ , and  $0.041352$  respectively. H. T. Kalmus and C. Harper gave  $R = 8.964 \times 10^{-6}$  ohm at  $18^\circ$  for 99.9 per cent. cobalt, and  $9.035 \times 10^{-6}$  for 98.71 per cent. cobalt previously heated to  $800^\circ$  in an atm. of carbon dioxide. H. Masumoto found  $11.83 \times 10^{-6}$  ohm at  $30^\circ$  for 99.46 per cent. cobalt, cast and annealed at  $800^\circ$ ; and K. Honda,  $8.59 \times 10^{-6}$  ohm at room temp. for 97.12 per cent. cobalt. J. C. McLennan and co-workers gave for purified cobalt heated 4 hrs. at dull redness in vacuo,  $6.85 \times 10^{-6}$  ohm at  $20^\circ$ , and when not so pre-heated,  $8.07 \times 10^{-6}$  ohm. L. Holborn said that the family iron, cobalt, and nickel is not only characterized by its ferromagnetism, but the *temperature coefficient* of the resistance is greater than with the other elements, being 0.003235 between  $-192^\circ$  and  $0^\circ$ ; 0.00658 between  $0^\circ$  and  $100^\circ$ ; 0.00475 between  $100^\circ$  and  $200^\circ$ ; 0.004096 between  $200^\circ$  and  $300^\circ$ ; and 0.003426 between  $300^\circ$  and  $400^\circ$ ; P. W. Bridgman found 0.0033 between  $0^\circ$  and  $100^\circ$ ; G. Reichardt, 0.00326 between  $0^\circ$  and  $150^\circ$ ; H. Copaux, 0.0055 between  $0^\circ$  and  $22^\circ$ , and 0.0060 between  $0^\circ$  and  $80^\circ$ ; and H. T. Kalmus and C. Harper, 0.00357 between  $0^\circ$  and  $100^\circ$ . A. Schulze gave for the temp. coeff. 0.00522 between  $15^\circ$  and  $25^\circ$ , and 0.00592 between  $0^\circ$  and  $100^\circ$ ; and for another sample the respective values 0.00303 and 0.00264 were observed. J. T. MacGregor-Morris and R. P. Hunt, E. van Aubel, W. Broniewsky, and A. Matthiesen and C. Vogt, made some observations on this subject. H. Schimank calculated for cobalt at absolute zero,  $R_0 = 0.8869$  ohm, and for the ratio  $R_r : R_0$  at  $273.09^\circ$  K.,  $194.4^\circ$  K.,  $81.8^\circ$  K., and  $20.2^\circ$  K., the respective values 1.0000, 0.7500, 0.4603, and 0.3920. W. Meissner and co-workers measured the resistance at temp. down to  $-271.8^\circ$ . If  $r$  denotes the ratio of the resistance  $R_r$  at the observed temp. to that of  $R_0$  at  $0^\circ$ ; and  $r_{\text{red}}$  denotes the estimated value for the pure metal, then for two different samples of purified cobalt: I, heated at  $500^\circ$  in vacuo; and II, melted in vacuo, when  $R_0$  for the former is  $1.604 \times 10^{-2}$  ohm, and for the latter,  $1.324 \times 10^{-4}$  ohm:

	$0.16^\circ$	$-184.84^\circ$	$-186.08^\circ$	$-194.60^\circ$	$-195.22^\circ$	$-252.59^\circ$	$-271.49^\circ$	$-271.84^\circ$
I { $r$ . . . . .	1	—	0.1829	—	0.1516	—	0.0431	—
{ $r_{\text{red}}$ . . . . .	1	0.1509	0.1465	0.1158	0.1139	0.00384	0.0000	—
II { $r$ . . . . .	1	0.1901	—	0.1588	—	0.05857	—	0.0624
{ $r_{\text{red}}$ . . . . .	1	0.1397	0.1355	0.1065	0.1047	0.0000	—	—

J. C. McLennan and co-workers gave for the resistance,  $R$  ohms, of aged and unaged cobalt:

	$20^\circ$	$-190^\circ$	$-252.4^\circ$	$-268.8^\circ$	$-270.5^\circ$
$R \times 10^3$ { Unaged . . . . .	1.80	0.495	0.313	0.277	—
{ Aged . . . . .	2.11	0.382	0.143	0.140	0.140

W. Tuijn and H. K. Onnes found that cobalt did not show superconductivity at low temp. W. Meissner studied the subject.

R. Ruer and K. Kaneko observed no perceptible effect was obtained on the electrical resistance of cobalt by heating it to  $1150^\circ$  in an atm. of nitrogen. According to H. T. Kalmus and C. Harper, the effect of annealing wires of purified cobalt in vacuo at  $350^\circ$  for several hours by passing an electric current through the wire, is to decrease the resistance about 5 per cent. This is not so much as for some metals, e.g. aluminium, for which H. Gwercke found a decrease of 10 per cent. by annealing for 2 hrs. at  $250^\circ$ . The effect of annealing in an atm. of carbon dioxide is at first to increase the resistance, and afterwards, as the temp. rises to  $800^\circ$ , the sp. resistance falls. A drop from  $10.1 \times 10^{-6}$  to  $9.35 \times 10^{-6}$  ohm per cm. cube, occurs in the sp. resistance of cobalt wire of a high degree of purity annealed

in an atm. of carbon dioxide at 600° compared with one similarly annealed at 500°. The difference in the effects of annealing in vacuo and in a gaseous atm. shows that the sp. resistance is largely influenced by adsorbed or occluded gases. Like copper, and most metals, the sp. resistance of cobalt is greatly augmented by the presence of impurities. Less than 0.5 per cent. of impurity may treble the electrical resistance. The electrical resistance of commercial cobalt wires, unannealed after swaging, varies between  $23.1 \times 10^{-6}$  and  $10.3 \times 10^{-6}$  ohm per cm. cube. The effect of annealing by passing a current through the wire in vacuo is to reduce the sp. resistance. Annealing for 5 hrs. at 350° reduced the sp. resistance 14 per cent.; and by heating in an atm. of carbon dioxide the resistance is decreased. There is a sharp decrease in the resistance in a sample annealed at 600° compared with one similarly annealed at 500°. With 99.6 per cent. cobalt, with a resistance  $R = 8.964 \times 10^{-6}$  ohm, at 18°, the values of  $R$ , after annealing 1 to 2 hrs. in an atm. of carbon dioxide, were :

Annealing temp.	400°	500°	600°	700°	800°
$R \times 10^6$	9.74 (17.7°)	10.11 (21.2°)	9.385 (15.4°)	9.333 (19.0°)	9.165 (16.5°)

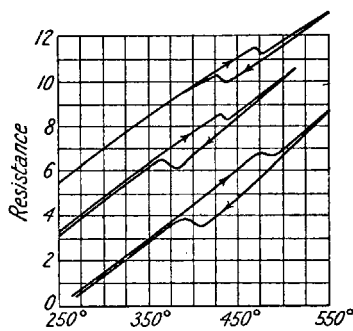
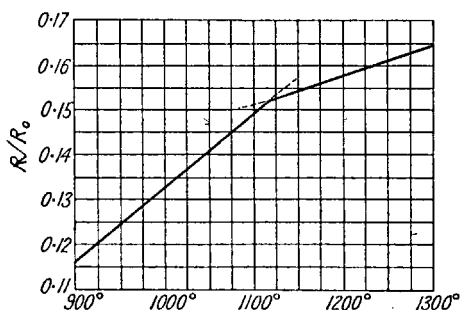
A. Schulze found the sp. resistance of cobalt of a high degree of purity to be  $R = 0.05636$  at 20°, and the temp. coeff. between 15° and 25° to be  $\alpha = 0.00522$ , and between 0° and 100°,  $\alpha = 0.00592$ . Between -192° and 500°, the temp. coeff. runs up from 0.00323 to 0.00592; falls down to 0.00342 with a maximum at about 50°; between 400° and 500°, there is a transition, and breaks occur in the temp. resistance curve at 444° and 468°, or :

	0°	100°	200°	300°	400°	500°
$R/R_0$	1.0000	1.5922	2.3540	3.3183	4.4552	5.4340

For temp. in the vicinity of the temp. of magnetic transformation, A. Schulze gave the results summarized in Fig. 14, where the resistance  $R_0$  at 0° is 0.057229 ohm, and for the ratio of the value  $R$  at  $\theta$  and the value at 0°, he gave  $R/R_0$  unity at 0°, and :

	1298°	1254°	1208°	1166°	1114°	1067°	1018.5°	965.1°	898.7°
$R/R_0$	16.322	16.123	15.812	15.554	15.062	14.377	13.535	12.738	11.661

H. Masumoto found that the variation of the electrical resistance with temp., using different samples of cobalt, is interrupted by an abrupt change as the temp. rises between 442° and 477°, Fig. 15; and during cooling, a reverse change occurs



FIGS. 14 and 15.—The Electrical Resistance of Cobalt.

at 360° to 403°. These changes correspond with the transition temp.; and this temp. is lowered by the presence of iron, etc. H. B. Peacock measured the resistance of thin films, and found the resistance of films 11 to 16  $m\mu$ , prepared by the condensation of the vapour, to be about 23 times its normal value; but if the films be preheated to 300° the normal value is obtained.

D. Foster compared the electrical and thermal conductivities. P. W. Bridgman

found that the effect of pressure is abnormally low; and he gave for the *pressure coefficient*:

	Resistance	Pressure Coefficient		
		At 0 kgrms.	At 12,000 kgrms.	Average 0 to 12,000 kgrms.
0°	1.0000	-0.0.941	-0.0.805	-0.0.873
50°	1.1825	-0.0.845	-0.0.755	-0.0.860
100°	1.3651	-0.0.745	-0.0.697	-0.0.726

A. Schulze also studied the effect of pressure. E. D. Williamson found the ratio of the resistance at 1 and 12,000 kgrms. per sq. cm. press. to be 0.9895. P. W. Bridgman observed that the effect of *tension* of 100 grms. on a cobalt wire 0.003 in. diam., is linear, with a tension coeff. of  $9.94 \times 10^{-7}$  at 30°, where the tension is measured in kgrms. per sq. cm. H. Tomlinson observed that the resistance of unannealed cobalt increases in a *magnetic field* by  $\delta R/R = 0.05628$  per unit magnetizing force; P. McCorkle observed  $\delta R/R = 0.004$  for  $H = 1000$  gauss. G. Fae said that the resistance of a thin plate increases if the plane of the plate is parallel to the lines of magnetic force, and decreases if the plate is vertical to those lines, and the subject was studied by D. Goldhammer, and Y. Matsuyama. L. Grunmach and F. Weidert studied the effect of transverse magnetization on the electrical conductivity of cobalt, and found that the percentage decrease produced by a field-strength of 10,000 gauss is -0.53. L. Bloch, F. Simon, K. Höjendahl, and K. F. Herzfeld discussed the theory of the electrical resistance. E. Branly found that a Ag-Mica-Co condenser shows unipolar conductivity only after a long-continued passage of the current.

P. E. Shaw<sup>23</sup> and co-workers studied the **tribo-electricity** of cobalt and glass; and W. A. D. Rudge, the production of negatively charged dust when cobalt is spluttered in air in a brass tube. J. B. Seth and co-workers studied the e.m.f. developed by cobalt and steel in contact and in relative motion. L. Bernoulli, V. Fredericksz, and A. Hesehus discussed the position of cobalt in Volta's **contact series**. C. Drucker placed cobalt in the **electrochemical series** . . . Zn, Fe, Cd, Tl, Co, Ni, Pb . . .; and B. Neumann, . . . Zn, Cd, Fe, Co, Ni, Pb . . . G. Tammann gave for the potential series with normal chlorides: Mg, Mn, Zn, Fe, Cd, Tl, Co, Ni, Pb, Sn, Cu, Bi, Ag, Au; and for the heats of formation of the solid chlorides, Mg, Mn, Zn, Cd, Tl, Pb, Fe, Sn, Co, Ni, Cu, Bi, Ag, Au. M. M. Haring and E. G. van den Bosche found that cobalt is more electropositive than nickel. The subject was discussed by A. S. Russell and co-workers, H. T. S. Britton, and C. B. Gates.

In its electrochemical behaviour, cobalt occupies a position between iron and nickel. The normal **electrode potential** of cobalt was reported by R. Abegg<sup>24</sup> and co-workers to be for  $\text{Co} \rightarrow \text{Co}^{++}$ , -0.29 volt; for  $\text{Co}^{++} \rightarrow \text{Co}^{+++}$ , 1.8 volt; and for  $\text{Co} \rightarrow \text{Co}^{+++}$ , 0.4 volt; and A. B. Lamb and A. T. Larson obtained for cobalt in a soln. of cobaltous chloride, -0.237 volt for  $\text{Co} \rightarrow \text{Co}^{++}$ ; and for  $\text{Co}^{++} \rightarrow \text{Co}^{+++}$ , they obtained 1.775 volts at 0°, 1.779 volts at 16°, and 1.817 volts at 25°, so that the temp. coeff. is 0.00169 volt. H. G. Denham and S. W. Pennycuik gave -0.247 volt; E. Müller and J. Janitzki, -0.292 volt; M. M. Haring and B. B. Westfall, -0.278 volt; and T. Heymann and K. Jellinek, -0.268 volt. Observations were also made by N. T. M. Wilshire, and M. le Blanc. G. Grube and O. Feucht obtained -0.52 volt for  $\text{Co} \rightarrow \text{CoO}_2^{++}$  against a soln. of potassium cobaltite in 8N-KOH; and A. S. Russell and co-workers obtained for passive cobalt, 0.8 volt. B. Neumann gave for the electrode potential of cobalt in a normal soln. of the sulphate, -0.255 volt; chloride, -0.259 volt; nitrate, -0.196 volt; and acetate, -0.207 volt. H. N. Huntzicker and L. Kahlenberg studied the potential in soln. of salts of copper, silver, and nickel.

W. Muthmann and F. Fraunberger observed that the potentials of the iron family of metals are sensitive to the presence of oxygen; and a cobalt activated cathode has a high potential, attaining -0.034 volt in  $N\text{-CoSO}_4$ , at 20°, and this is the so-called air potential by cobalt. By polishing a cobalt rod, the potential

changes from  $-0.034$  volt to  $-0.264$  volt, and after lying in air a few seconds,  $-0.074$  volt. After treatment cathodically in potash lye, the potential is  $-0.234$  volt; when treated with conc. chromic acid,  $-0.076$  volt; when treated as anode in a soln. of potassium thiocyanate,  $-0.104$  volt; potassium cyanide,  $-0.074$  volt; distilled water,  $-0.074$  volt; and potash lye,  $0.746$  volt. G. Coffetti and F. Förster observed that a freshly-fractured electrolytic cobalt has, after a short time, the potential  $-0.25$  volt in  $N\text{-CoSO}_4$  at  $20^\circ$ , and this value is independent of the conc. of the  $\text{Co}^{++}$  ions, so that the value is not dependent on the equilibrium  $\text{Co} \rightleftharpoons \text{Co}^{++}$ . R. Schildbach observed that the electrode potentials of cobalt powder in an atm. of nitrogen against  $N\text{-CoCl}_2$  and  $0.1N\text{-CoCl}_2$  are respectively  $-0.293$  and  $-0.339$  volt; and against  $N\text{-CoSO}_4$  and  $0.1N\text{-CoSO}_4$ , respectively  $-0.316$  and  $-0.339$  volt compared with a normal hydrogen electrode. The sign refers to the cobalt electrode. With massive cobalt, the values are rather more positive—e.g., with  $N\text{-CoSO}_4$ , it is  $-0.288$  volt. Cobalt powder charged with hydrogen gives considerably more negative values at first, which gradually change until the equilibrium potential is reached. When unpolarized cobalt is placed in a cold soln. of one of its salts, its potential is more positive than the equilibrium value,  $-0.121$  volt, for example, but the equilibrium value is reached fairly quickly. Thus:

Time	2	7	22	42	66	140	240 mins.
E	$-0.158$	$-0.216$	$-0.247$	$-0.284$	$-0.310$	$-0.319$	$-0.319$ volt

From neutral soln., in an atm. of hydrogen, cobalt is deposited with quantitative current efficiency. The difference of potential between the electrode and the electrolyte is, however, much larger than the equilibrium value. The difference increases with the current density, and diminishes as the temp. rises, almost vanishing at  $90^\circ$ ; it is very much increased by the addition of small quantities of acid to the soln., and this effect is especially marked at a low temp. The subject was studied by M. M. Haring and E. G. V. Bosche.

E. Newbery found that the electrode potential of cobalt at  $15^\circ$ , under conditions where the effects due to occluded hydrogen are excluded, is  $0.22$  volt for  $0.1N\text{-CoSO}_4$ ,  $0.21$  volt for  $0.1N\text{-Co(NO}_3)_2$ , and  $0.15$  volt for  $0.1N\text{-CoCl}_2$ . The low values for cobaltous chloride were attributed to the formation of a complex salt; and R. Abegg and S. Labendzinsky came to a similar conclusion. E. Newbery observed that the potential in the sulphate or nitrate soln. attains a constant value in a few hours owing to some surface change. When the soln. are stirred, the potential in sulphate soln. rises  $0.13$  volt, and in chloride soln.,  $0.07$  volt; and when the stirring has ceased, the potential returns to its original value—at first rapidly and then slowly. G. B. Bonino and M. Bottini found that the potential of finely-divided cobalt electrolytically deposited on platinum, towards distilled water, rises in 16 hrs. from  $-0.625$  volt to the constant value  $-0.705$  volt. W. Muthmann and F. Fraunberger gave for the potential in soln. of potassium hydroxide (1 : 3),  $-0.024$  volt; 30 per cent. chromic acid,  $0.456$  volt; 10 per cent. sulphuric acid,  $-0.124$  volt; and 34 per cent. nitric acid,  $0.226$  volt. S. J. French and L. Kahlenberg measured the potential in  $N\text{-KCl}$ , and found that in hydrogen, the potential becomes more basic, reaching a maximum and then falling off; in nitrogen, the potential becomes more basic, and attains a maximum; and in oxygen, the potential becomes less basic, reaching a maximum and then falling off in bubbling gas, but it becomes more basic with the gas quiescent. L. Kahlenberg and J. V. Steinle observed the single potentials of cobalt in a soln. of  $0.5N\text{-Na}_3\text{AsO}_4$  to be  $0.127$  volt; in  $0.5N\text{-K}_3\text{AsO}_4$ ,  $0.131$  volt; and in  $N\text{-KCl}$  sat. with arsenic trioxide,  $0.126$  volt. W. Hiltner and W. Grundmann studied the electrometric titration of the sulphate.

S. Labendzinsky found the **electromotive force** of the combination  $\text{Co} : 0.5N\text{-CoCl}_2$  and  $N\text{-KCl}$  against  $\text{Hg}_2\text{Cl}_2 : \text{Hg}$ ,  $0.592$  volt; with  $0.05N\text{-CoCl}_2$ ,  $0.625$  volt; with  $0.5N\text{-CoSO}_4$  and  $N\text{-Na}_2\text{SO}_4$ ,  $0.622$  volt; and with  $N\text{-Co(NO}_3)_2$  and  $N\text{-KNO}_3$ ,  $0.588$  volt. R. Schildbach studied some combinations with cobalt,



$N\text{-}0\cdot1N\text{-CoSO}_4$  or  $\text{CoCl}_2$ , and a sat. soln. of potassium chloride and the calomel electrode, and of the cells  $\text{Co} : \text{CoSO}_4 : N\text{-Na}_2\text{SO}_4 : \text{CuSO}_4 : \text{Cu}$ . A. B. Lamb and A. T. Larson found for the combination  $\text{Co} : M\text{-CoCl}_2 : N\text{-KCl}, \text{Hg}_2\text{Cl}_2 : \text{Hg}$ , at  $25^\circ$ :

$M$	.	.	0.01	0.02	0.05	1.0	2.0
$E$	.	.	0.582	0.570	0.556	0.539	0.525 volt

They also measured combinations with the cobalt chloride mixed with aq. ammonia; and H. G. Denham and S. W. Pennycuik, combinations with the cobalt chloride associated with potassium, magnesium, zinc, and aluminium chlorides. V. Regnaud studied the cell  $\text{Co}$  and  $\text{HNO}_3$  and a cobalt salt against sulphuric acid and zinc amalgam and zinc. F. Streintz studied cells with cobalt and an aq. soln. of cobalt salt against a metal salt soln. and the corresponding metal—copper, silver, magnesium, zinc, cadmium, tin, and bismuth. B. Neumann observed with cobalt and a  $N$ -cobalt salt against a  $N$ -soln. of an indifferent electrolyte,  $N\text{-KCl}$  and  $\text{Hg}_2\text{Cl}_2$ , and mercury, the sulphate gave 0.541 volt; the chloride, 0.545 volt; the nitrate, 0.480 volt; and the acetate, 0.556 volt; W. Muthmann and F. Fraunberger studied cells with  $N\text{-KCl}, \text{Hg}_2\text{Cl}_2$  and mercury against cobalt and soln. of cobalt sulphate; potassium chloride, hydroxide, cyanide or thiocyanate; or sulphuric, hydrochloric, nitric or chromic acid; G. Coffetti and F. Förster, the cell  $\text{Co} : N\text{-CoSO}_4 : 0\cdot1N\text{-KCl}, \text{Hg}_2\text{Cl}_2 : \text{Hg}$ . A. von Oettingen, and S. B. Christy, the cell  $\text{Co} : N\text{-KCy} : N\text{-KCl}, \text{Hg}_2\text{Cl}_2 : \text{Hg}$ ; and K. Zengelis,  $0\cdot1N\text{-KCl} : N\text{-KCl}, \text{Hg}_2\text{Cl}_2 : \text{Hg}$  against cobalt and a soln. of cobalt sulphate and  $0\cdot1N$ -soln. of potassium sulphide, aq. ammonia, potassium nitrite, sodium phosphate, potassium arsenate, or potassium cyanide. W. Hittorf examined cells with platinum and chromic acid against cobalt and soln. of sodium nitrate, sulphate, or acetate, or potassium dichromate. H. W. Toepffer found for the cell  $\text{Co} : \text{CoSO}_4$  against  $\text{NiSO}_4 : \text{Ni}$ , 0.26 volt, and against  $\text{FeSO}_4 : \text{Fe}$ , 0.13 volt; for  $\text{Co} : \text{CoSO}_4$  and  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  against  $\text{NiSO}_4(\text{NH}_4)_2\text{C}_2\text{O}_4$  and nickel, —0.25 volt, and with iron in place of nickel—salt and metal—0.21 volt; and for  $\text{Co} : \text{CoSO}_4$  and  $(\text{NH}_4)_2\text{SO}_4$  against nickel and ammonium sulphate and nickel, —0.19 volt, and with iron in place of nickel—salt and metal—0.18 volt. Observations were also made by E. Oberer, K. Georgi, and N. P. Kazankin. G. B. Bonino and co-workers studied cells with cobalt against a cobalt salt and protein, egg-albumin, or blood-serum, against platinum. H. J. Blik-slager studied cells with cobalt against cobalt chloride and an alkali chloride against molten alkali chloride with a different proportion of cobalt chloride. A. C. Krueger and L. Kahlenberg studied the cells with cobalt and a soln. of gas in an electrolyte against the normal calomel electrode at  $22^\circ$  to  $24^\circ$ , and found:

	$\text{H}_2$	$\text{O}_2$	$\text{N}_2$	A	He
$N\text{-KCl}$	0.598	0.457	0.581	0.560	0.553
$N\text{-KOH}$	0.885	0.832	0.866	0.888	0.896
$N\text{-HCl}$	0.447	0.382	0.439	0.444	0.438

The **ionic mobility** of cobalt for  $\frac{1}{2}\text{Co}^{++}$ , was found by A. Heydweiller to be 43.0 at  $18^\circ$ ; E. Rona gave 47.7 at  $18^\circ$ ; A. Feiler, 51.0 at  $18^\circ$ ; W. Riedel gave for soln. with a mol per 20.8, 203.5, and 432 litres the respective values 0.6218, 0.6062, and 0.6040; W. Althammer gave 50.6 for the chloride, 51.4 for the bromide, and 50.9 for the iodide at  $20^\circ$  respectively for chloride, bromide and iodide soln.; and C. Mazzetti gave:

	$10^\circ$	$20^\circ$	$30^\circ$	$40^\circ$	$50^\circ$	$60^\circ$
Ionic mobility	46	73	102	124	144	155

R. C. Cantelo and E. C. Payne gave 0.396 for the transport number of the  $\text{Co}^{++}$ -ion in  $0\cdot233N\text{-CoSO}_4$ , and 0.149 in  $3\cdot994N\text{-CoSO}_4$ . W. C. D. Whetham calculated the absolute velocity of the ions for a fall of potential of 1 volt per cm. to be  $0\cdot0_422$  cm. per sec. for soln. of cobaltous chloride in alcohol; and  $0\cdot0_444$  cm. per sec. for alcoholic soln. of cobaltous nitrate. E. Gapon, and E. Newbery discussed the **hydration of the ions** of cobalt. W. Ostwald calculated the **heat of ionization**,  $\text{Co} \rightarrow \text{Co}^{++}$ , to be

73 kilojoules on the assumption that the heat of ionization  $H_2=2H^+$  is zero. J. D. Bernal and R. H. Fowler calculated for the **ionization energy** of the  $Co^{++}$ -ion, 594 Cals. per gram-ion.

According to C. Luckow, when a neutral soln. of a cobalt salt is electrolyzed, cobalt is incompletely separated, but if acetic acid be present, or, according to A. Riché, if other acids be present, the separation is complete. A large excess of acid, however, hinders the electrodeposition of cobalt; but it is favoured by the presence of alkali acetates, citrates, tartrates, or oxalates; or of potassium cyanide, or sodium hydrophosphate, or pyrophosphate. This subject was studied by H. Kersten, and A. Job—*vide supra*, the extraction of cobalt. According to F. W. Skirrow, when a hydrofluoric acid soln. of a cobalt salt is electrolyzed, cobaltic oxide is formed, but this is not the case in sulphuric acid soln. He showed that the oxidizing action at the anodic depends on the potential. A. Coehn and co-workers observed that in dil. alkaline soln., anodic oxidation occurs with cobalt sulphate at 1.21 volts and with nickel sulphate at 1.3 volts; in dil. acidic soln., the oxidation occurs with cobalt sulphate at 1.52 volts, and not with nickel sulphate soln.; and in conc. acidic soln., the anodic oxidation does not occur.

M. le Blanc found the **deposition potential** of cobalt from  $N-CoSO_4$  to be  $-0.444$  volt, and G. Coffetti and F. Förster showed that in order to prevent the formation of hydroxide, at  $20^\circ$ , the soln. must be acidified. With a voltage of  $-0.55$  to  $-0.61$ , and a current density,  $D$  amp.  $\times 10^{-4}$  per sq. cm.:

Current Density	11.3	22.7	45.5	93.0	182.0
$N$ -Acid	0.0025	0.005	0.0075	0.01	0.02
Current yield	29	68	70.5	76.5	66 to 70 per cent.

R. Schildbach showed that in these observations the oxygen of the air should be excluded, since it acts as a depolarizer on the cathodic hydrogen. S. Glasstone studied the effect of the current density on the cathode potentials of cobalt in  $N-CoSO_4$  at  $15^\circ$ , and found for current densities of  $D$  amp.  $\times 10^{-4}$  per sq. cm.:

$D$	$0.1N-H_2SO_4$	$P_H=2.8$	$P_H=4.0$	$P_H=5.0$	$P_H=6.0$
0.14	-0.19	-0.17	-0.19	-0.22	-0.24
0.56	-0.22	-0.22	-0.34	-0.39	-0.44
1.4	-0.31	-0.42	-0.49	-0.56	-0.56
2.8	-0.36	-0.46	-0.56	-0.57	-0.57
5.6	-0.42	-0.51	-0.57	-0.59	-0.59
12.0	-0.49	-0.56	-0.59	-0.61	-0.61
40.0	-0.56	-0.57	-0.61	-0.62	-0.63
80.0	-0.57	-0.59	-0.62	-0.63	-0.64
160.0	-0.58	-0.60	-0.63	-0.64	-0.65

R. Schildbach studied the effect of current density and temp. on the deposition potential, and found, for neutral, and normal soln.:

$D$		0.4	1.4	5.7	22.7	45.5	182
$E \left\{ \begin{array}{l} N\text{-CoCl}_2 \\ N\text{-CoSO}_4 \end{array} \right.$	$\left\{ \begin{array}{l} 1^\circ \\ 20^\circ \\ 50^\circ \\ 92^\circ \end{array} \right.$	—	-0.413	-0.431	-0.455	-0.474	-0.533
		-0.361	-0.370	-0.380	-0.398	-0.414	-0.459
		—	-0.335	-0.338	-0.345	-0.354	-0.390
		—	—	—	—	-0.294	-0.337
	$\left\{ \begin{array}{l} 1^\circ \\ 20^\circ \\ 50^\circ \\ 92^\circ \end{array} \right.$	—	-0.405	-0.433	-0.466	-0.486	-0.562
		—	—	-0.390	-0.410	-0.428	-0.498
		—	-0.324	-0.340	-0.363	-0.374	-0.427
		—	—	—	-0.306	-0.315	-0.359

and also the effect of acidity and temp. With  $N-CoCl_2$ , the deposition potentials were:

		Neutral	0.5 per cent. $H_3BO_3$	2 per cent. $H_3BO_3$	0.003N-HCl	0.03N-HCl
$E \begin{cases} 1^\circ \\ 20^\circ \\ 50^\circ \\ 75^\circ \end{cases}$	$1^\circ$	-0.474	0.153	0.141	0.119	0.125
	$20^\circ$	-0.415	0.061	0.129	0.132	0.110
	$50^\circ$	-0.354	-0.004	0.012	0.072	0.070
	$75^\circ$	-0.317	-0.007	-0.001	0.043	0.054

Similar results were obtained with soln. of cobalt sulphate. The subject was also discussed by G. Devoto and A. Ratti, H. Stäger, F. Förster, E. Vogel, J. Heyrovsky, P. K. Frölich and G. L. Clark, S. Sartori, and G. Grube. R. Brdicka found that the deposition potential from soln. of cobaltous chloride becomes more positive as the concentration of the added calcium chloride increases. The ionic valency of cobalt in pink soln. is two-thirds, and in blue soln., it is 2. Cobalt deposits reversibly from blue soln., *i.e.* soln. containing about 10*N*-CaCl<sub>2</sub> at room temp., or, at 100°, 5*N*-CaCl<sub>2</sub>. The cathodic deposition potential of cobalt from blue soln. is about 0.3 volt more positive than it is from pink soln. with the same concentration of cobalt. The Co<sup>++</sup>-ions are therefore more active in the blue soln. The irreversible deposition of cobalt from the pink soln. is attributed to the slow dehydration of the pink hydrated ions; and the reversible deposition from blue soln. is attributed to the ease of splitting the blue into dehydrated free Co<sup>++</sup>-ions—*vide infra*, the deposition potential of nickel. S. Glasstone studied the simultaneous electro-deposition of zinc and cobalt. He found the electrodeposition potential and over-voltage in *N*-soln. to be respectively -0.56 and 0.25 volt at 15°; -0.46 and 0.15 volt at 55°; and -0.36 and 0.05 volt at 95°.

The **cathodic or hydrogen overvoltage**, or the minimum voltage for the first visible appearance of hydrogen with a cobalt electrode in *N*-H<sub>2</sub>SO<sub>4</sub>, at 20°, was found by W. D. Harkins to be  $E=0.22$  volt; with finely-divided cobalt, 0.5*N*-H<sub>2</sub>SO<sub>4</sub>, at 20°; M. Centnerszwer and M. Straumanis gave  $E=0.29$  volt; and with cobalt deposited on platinum in 0.01*N*-H<sub>2</sub>SO<sub>4</sub>, A. Thiel and W. Hammerschmidt gave  $E=0.29$  volt, and on silver,  $E=0.064$  volt. The galvanic polarization of cobalt was studied by E. Vogel; and the separation of hydrogen at the cobalt cathode by I. Slendyk and P. Herasymenko. N. Thon studied the subject. U. C. Tainton found that a high current density increases the hydrogen overvoltage with cobalt chloride soln. G. Carrara observed that at 19° to 20°, with smooth electrodes and *N*-H<sub>2</sub>SO<sub>4</sub> in water, methyl alcohol, and ethyl alcohol, the respective hydrogen overvoltages were 0.25, 0.20, and 0.27 volt. N. Isgarischeff and H. Ravikovitsch, and E. Newbery studied the **cathodic polarization**, and the latter observed that the electrode potential of cobalt in *N*-CoSO<sub>4</sub> is 0.22 volt; in *N*-Co(NO<sub>3</sub>)<sub>2</sub>, 0.21 volt; and *N*-CoCl<sub>2</sub>, 0.15 volt. The cathodic overvoltage of cobalt with current densities *D* milliamps. per sq. cm. in normal soln. is:

Current Density	2	6	10	20	50	100	200	400
CoSO <sub>4</sub>	0.50	0.48	0.48	0.48	0.50	0.51	0.51	0.49
Co(NO <sub>3</sub> ) <sub>2</sub>	0.26	0.38	0.45	0.57	0.73	0.72	0.69	0.64
CoCl <sub>2</sub>	0.31	0.30	0.31	0.32	0.35	0.38	0.44	0.53
H <sub>2</sub> SO <sub>4</sub>	0.27	0.28	0.28	0.27	0.27	0.26	0.26	0.25
NaOH	0.25	0.28	0.28	0.29	0.29	0.29	0.30	0.30

The cathodic overvoltage resembles that of nickel but is more constant, being less liable to change with time or current density. In alkaline soln., at first the over-voltage is little higher than that of nickel, but gradually rises with time. At very high current densities, sudden rapid rises of overvoltage take place, sometimes directly the current density reaches a high value, and at others, after repeatedly raising and lowering the current density between the limits 2 and 2000 milliamperes per sq. cm. This rise may be as much as 0.4 volt, and after it has taken place the high overvoltage persists at all current densities, the metal then behaving like a new electrode, such as lead or zinc. Cleaning with glass-paper at once restores the normal overvoltage; hence the effect is purely a surface one and is probably due to the formation of a cobalt alloy.

J. Nickles observed that if cobalt be superficially oxidized by heat, it assumes the **passive state** in fuming nitric acid; and St. Edme found that whilst cobalt always dissolves in the conc. acid without becoming passive, the cold, dil. acid does not attack the metal. E. Ramann attributed the passivity of cobalt to the formation of a protective film on the surface of the metal. W. W. Hollis said that

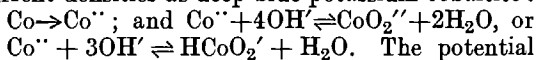
the passivation of cobalt by fuming nitric acid depends on the texture of the metal, the time of action, and the temp. The critical temp. above which the passive state disappears is about  $10^{\circ}$ . R. Schildbach observed that with soln. of cobalt chloride or sulphate, no passivation of cobalt was detected with current densities up to  $182 \times 10^{-4}$  amp. per sq. cm., and at temp. up to  $92^{\circ}$ . E. Newbery found that at  $15^{\circ}$ , and a current density of 0.4 amp. per sq. cm., cobalt does not become passive in *N*-soln. of cobalt chloride, nitrate, or sulphate; W. Hittorf observed the passivation of anodic cobalt in soln. of potassium dichromate, or sodium acetate; and H. G. Byers, in soln. of potassium carbonate or dichromate. E. S. Hedges observed that the presence of sulphuric acid or sodium sulphate hinders the passivation of cobalt in soln. of potassium dichromate; and cobalt is passivated in 0.5*N*- $\text{H}_2\text{SO}_4$  with a current density exceeding 0.16 amp. per sq. cm.; in 0.2*N*- $\text{Na}_2\text{SO}_4$ , by a current density exceeding 0.24 amp. per sq. cm., and in a 20 per cent. soln. of potassium cyanide, cobalt is immediately passivated. H. G. Byers found a current density of 0.84 amp. per sq. cm. is necessary to develop oxygen in *N*- $\text{NaNO}_3$ ; and one of 4 to 5 amp. per sq. cm. in *N*- $\text{NaHCO}_3$  and in *N*- $\text{KMnO}_4$ . W. Muthmann and F. Fraunberger, and C. Fredenhagen discussed the electrode potential of passive iron and cobalt, and they concluded that the anodic oxygen depresses the speed of the reaction with the metal and itself to such an extent that the anode is covered completely with a layer of oxygen, or that an alloy of metal and oxygen is formed which prevents further action, and so produces the passive state. H. G. Byers added that these negative potentials are due to the oxygen electrode and increase or decrease with the conc. of the oxygen; but they do not account for the passive state of iron in potassium cyanide and other reducing agents. G. Grube and O. Feucht found that passive cobalt is activated by cathodic polarization. E. Müller and F. Spitzer observed that in many cases the production of the passive state is accompanied by the formation of a film of oxide. The subject was studied by G. C. Schmidt, U. R. Evans, W. J. Müller, and E. Becker and H. Hilberg. According to E. Newbery, unlike nickel, cobalt cannot be passivated in dil. sulphuric acid with an electric current. Passivity, however, is readily produced in alkaline soln. W. Frese studied the effect of films on the photo-electric properties and on passivity; and A. S. Russell, the electronic structure of metals in the passive state. A. Smits and A. H. W. Aten observed that the potential of cobalt is raised by etching with hydrochloric, sulphuric, or nitric acids, and hence they attributed passivity to the existence of an allotropic modification of the metal in the surface layers—*vide* the passivity of iron. H. G. Byers, and E. S. Hedges, studied the periodic passivity of cobalt; U. Sborgi and A. Borgia examined the action of a magnetic field on passivity.

H. G. Byers and C. W. Thing showed that a cobalt anode becomes passive if the current density is sufficiently high. The passive state is indicated by an increased drop in the voltage, a decreased current, the evolution of oxygen, and the resistance of the metal to dissolution. The essential difference between cobalt and iron or nickel is that cobalt does not become passive at the low current densities required by nickel and iron. If cobalt assumes the passive state, it remains so even when the current density is reduced; and cobalt becomes active in acidic soln. more readily than is the case with nickel. H. G. Byers added that the anodic behaviour of cobalt containing some nickel is not very different from that of cobalt alone.

J. C. Poggendorff observed that the cell with a cobalt anode  $\text{Co} : \text{KOH} : \text{HNO}_3 : \text{Pt}$  develops oxygen without forming a film oxide on the cobalt. According to C. Tubandt, cobalt is not attacked by a hot or cold soln. of potassium or sodium hydroxide, but when exposed as anode to an electric current, it dissolves in the alkali lye. The most favourable conditions for the dissolution are a low current density—0.2 amp. per sq. dm.—high temp., and a highly conc. soln. of lye. The cobalt dissolves as a cobaltous salt. The cobaltous soln. is blue, and in absence of air is stable for months. When electrolyzed between insoluble electrodes, it

precipitates part of the cobalt at the cathode as spongy metal, part at the anode as oxide; the chief part is oxidized by the oxygen given off at the anode, and the oxidation product remains suspended in the form of brown flecks in the electrolyte. F. Förster and A. Piquet observed that with  $2N$ -KOH, at  $15^\circ$ , and a current density of  $0.333$  amp. per sq. cm., cobalt is attacked more strongly than iron, and a layer of hydrated cobaltic oxide may be formed on the metal. E. Newbery said that cobalt is passive in  $N$ -NaOH with a current density of  $2$  to  $1200$  milliamp. per sq. cm.; H. G. Byers, that in  $N$ -KOH and  $5$  milliamp., no loss in weight occurs; and F. Förster, that with  $10N$ -KOH, and  $0.3$  milliamp. per sq. cm. at  $60^\circ$ , or  $0.8$  milliamp. per sq. cm. at  $80^\circ$ , a cobalt anode remains active, but with the same current densities respectively at  $40^\circ$  and  $60^\circ$ , passivity sets in as an oxide layer is formed. K. Georgi studied the anodic behaviour of cobalt.

G. Grube and O. Feucht found that with conc. soln. of potassium hydroxide, anodic cobalt dissolves at high current densities as deep-blue potassium cobaltite:



The potential measurements show that the blue compound in  $8N$ -KOH is potassium cobaltite,  $\text{K}_2\text{CoO}_2$ , and not colloidal cobaltous hydroxide. The normal potential of cobalt against potassium cobaltite is  $-0.52$  volt. Fig. 16 shows that there are two stages in the potential current density curves; the first stage occurring with potentials between  $-0.3$  and  $-0.6$  volt. Here the cobalt is active; no oxygen is evolved at the anode; and with highly conc. alkali-lye, the blue soln. is formed, but with more dil. alkali-lye, an oxide is formed on the electrode or in the electrolyte. In the second stage, the cobalt no longer dissolves, and oxygen is developed.

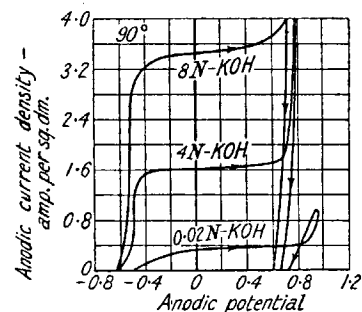


FIG. 16.—The Current Density-Potential Curves of Cobalt in Potash-Lye.

The anodic oxidation of a soln. of the cobaltite, at platinum occurs in three stages: (i) at low potentials, cobaltous oxide is formed; (ii) at medium potentials, cobaltic oxide is produced; and at high potentials, a solid soln. of cobalt dioxide in one of the lower oxides is formed and the evolution of oxygen occurs. In the electrolytic evolution of oxygen at cobalt anodes in alkali hydroxide the cobalt first unites with the charged atomic oxygen forming cobalt dioxide, and this decomposes into cobaltic oxide and molecular oxygen. For G. Grube's observations on the polarization of cobalt in alkaline soln. of potassium ferrocyanide and ferricyanide, *vide* iron. A. P. Rollet discussed the anodic reactions of cobalt in acidic or alkaline soln.

U. Sborgi and G. Cappon found that cobalt dissolves in an ethyl alcohol soln. of calcium and ammonium nitrates as a bivalent ion at all current densities from  $0.03$  to  $3.0$  amp. per sq. dm.; and U. Sborgi and P. Marchetti found that cobalt forms bivalent ions in an acetone soln. of lithium chloride, and becomes passive in an acetone soln. of silver nitrate. N. Isgarischeff observed that the e.m.f. of cobalt in a  $0.177N$ -soln. of cobalt chloride in ethyl alcohol, increases rapidly until the metal becomes passive; the potential remains unchanged at  $0.03$  volt against a H-electrode, and the smooth and white surface of the metal becomes matte with a yellow tinge. If the metal be removed and cleaned, it has its original potential when again immersed in the liquid, but the passive state is acquired more quickly than before, and on repeating the process, the rate at which the metal becomes passive continues to increase. If all the oxygen be removed from the soln., and observations made in a current of hydrogen, the potential remains constant,  $-0.174$  volt, and there are no signs of passivation. The passivation in these organic solvents is thus attributed to the presence of a soluble substance of the nature of a peroxide, and the case of passivation of cobalt in alcoholic soln. is attributed to the formation of an oxide coating on the metal. N. Kondyreff observed that in a soln.

of ethyl bromide, in dry ether, cobalt does not dissolve anodically and no complex salt is formed. L. F. Audrieth and L. F. Yntema studied the electrodeposition of cobalt from solutions of the nitrate in liquid ammonia.

According to W. Hittorf, cobalt dissolves and is active when employed as anode in dil. soln. of sulphuric acid, sulphates, or nitrates; and in soln. of nitric acid of sp. gr. 1.2, H. G. Byers found a cobalt anode is dissolved in *N*-soln. of nitric, acetic, oxalic, and citric acid at room temp., and current density of  $D=0.5$  amp. per sq. dm., and the dissolution of cobalt occurs at room temp. with the following values of  $D$ : *N*-NaCl, 0.5; *N*-CuCl<sub>2</sub>, 1.0; *N*-KCl, 0.5; *N*-KNO<sub>3</sub>, 1.0; 0.1*N*-KNO<sub>3</sub>, 0.5; sat. soln. NaNO<sub>2</sub>, 3.6; sat. soln. NaNO<sub>3</sub>, 8.4; *N*-Na<sub>2</sub>SO<sub>4</sub>, 0.5; *N*-CoSO<sub>4</sub>, 1.0; *N*-Na<sub>2</sub>CO<sub>3</sub>, 0.5; *N*-NaHCO<sub>3</sub>, 0.5; *N*-K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, 0.8; *N*-NaH<sub>2</sub>PO<sub>4</sub>, 0.5; *N*-KMnO<sub>4</sub>, 0.4; and *N*-KClO<sub>3</sub>, 0.5. Cobalt dissolves anodically in fuming nitric acid at 0°; and, according to E. Newbery, in *N*-HCl, while cobalt is not passive in *N*-H<sub>2</sub>SO<sub>4</sub> at 15° and 2 amp. per sq. cm., at very high current densities, its potential approaches that of the oxygen electrode. E. S. Hedges said that cobalt is not passive in 0.05 to 20 per cent. hydrochloric acid; in 0.5 to 100 per cent. nitric acid; in 1 to 10 per cent. ammonium sulphate; or in 2 to 10 per cent. sodium sulphate. With small current densities, cobalt forms a red soln. with 50 vol. per cent. sulphuric acid, and a green soln. with high current densities. According to H. G. Byers and C. W. Thing, when cobalt is active and no current is flowing through the electrode, it has a negative potential, but when the electrode is an anode, and a current is flowing, the potential changes in sign, and increases in value even if the metal remains active. If the metal becomes passive, the potential is much increased. Thus, at 0°, against a normal calomel electrode :

		Potential		State of Metal
		without current	with current	
0.2 <i>N</i> -H <sub>2</sub> SO <sub>4</sub>	{ Cobalt— 98 per cent. .	-0.350	+0.605 to 0.671	Active
	{ Cobalt— 98 „ .	-0.278	+1.888 to 1.849	Passive
	{ Cobalt— 98 „ .	-0.411	+0.270 to 0.250	Active
0.2 <i>N</i> -Na <sub>2</sub> SO <sub>4</sub>	{ Cobalt— 98 „ .	-0.411	+1.811 to 1.824	Passive
	{ Cobalt—100 „ .	-0.416	+0.302 to 0.264	Active
	{ Cobalt—100 „ .	-0.416	+1.870 to 1.840	Passive
0.2 <i>N</i> -K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	{ Cobalt—100 „ .	-0.306	+2.422 to 2.522	Passive

According to A. Coehn and Y. Osaka, the **oxidation potential** of cobalt is 0.85 volt against a constant hydrogen electrode, and oxygen is evolved at 1.36 volts. A. Coehn and M. Gläser found that in a slightly alkaline soln., cobalt shows an anodic formation of oxide at 1.21 volts; in a slightly acidic soln., at 1.52 volts; and in a strongly acidic soln., no oxide is formed. The oxide deposited in thin layers is Co<sub>2</sub>O<sub>3</sub>.2H<sub>2</sub>O, and in thick layers, Co<sub>2</sub>O<sub>3</sub>.3H<sub>2</sub>O. Cobalt can be completely deposited as peroxide on the electrolysis of a dil. soln. with a current of 0.1 ampere, and 2.3 to 2.4 volts. A long time is required, and the method is not a convenient one for separating cobalt and nickel. E. Newbery observed the **oxygen or anodic overvoltage** of cobalt for current densities  $D$  milliamp. per sq. cm. :

Current Density	2	6	10	20	50	100	400	1200
NaOH . . .	0.58	0.60	0.59	0.58	0.58	0.57	0.56	0.54
CoSO <sub>4</sub> . . .	0.02	0.03	0.03	0.04	0.05	0.06	0.06	0.08
Co(NO <sub>3</sub> ) <sub>2</sub> . .	0.11	0.11	0.09	0.06	0.00	0.00	0.02	0.02
CoCl <sub>2</sub> . . .	0.03	0.02	0.00	-0.02	-0.03	-0.02	+0.03	+0.07

E. Newbery added that the anodic overvoltage is low and fairly constant, and has similar values in acidic and alkaline soln. It shows a tendency to fall slightly with time. F. Förster gave for the anodic potential of a cobalt electrode in *N*-KOH as the current density changes from 0 to  $3 \times 10^{-4}$  amp. per sq. cm.,  $E=0.7$  volt to about 0.92 volt. E. Müller and F. Spitzer said that at first the anodic potential rises gradually, and attains its end-value in about an hour with spongy cobalt, and in about 3 hrs. with polished cobalt. In 2*N*-NaOH, and a current density of 0.03 amp. per sq. cm., the end-value against a calomel electrode is 0.580 volt for

burnished cobalt, 0.476 volt for spongy cobalt, 0.477 volt for cobalt oxide, and 1.416 volt for platinum. The agreement between the values for cobalt oxide indicates that a layer of oxide is formed on the metal. The measurement of the anodic overvoltage was discussed by E. Newbery, A. D. Garrison and J. F. Lilly, and M. Knobel; the use of cobalt as an anode in electrolysis, by E. A. Benjamin, R. Saxon, J. H. Levin, and C. G. Fink. E. Müller and J. Janitzki observed that when the metal is rubbed, and immersed in soln. of acids, bases, or neutral salts, the electrode potential is nearly reversible. The use of the tungsten-cobalt couple for electrometric titrations was described by A. C. Krueger and L. Kahlenberg, and M. L. Holt and L. Kahlenberg; and the use of cobalt electrodes in reducing a soln. of barium nitrate to nitrite, by P. Wenger and A. Lubomirsky.

P. Bechtereff measured the anodic potential of cobalt in molten sodium hydroxide between 330° and 650°, and from its resemblance to the values for nickel, iron, and the noble metals, he concluded that a gas potential is actually measured. A. Günther-Schulze measured the **electrolytic valve action** of cobalt. A. P. Rollet found that in the electrolysis of dil. soln. of alkali lye, or dil. sulphuric acid, with an alternating current, the electrodes of cobalt are alternately covered with oxide, and powdered metal.

According to T. de Grotthus, when an electric current is passed through two soln. of silver nitrate communicating with each other by a crack in a glass tube containing one of them, and the positive pole is immersed in the external vessel, silver is deposited on the outside of the crack, and oxygen is given off inside. F. Braun showed that the phenomenon occurs with cobalt, iron, lead, gold, and palladium, but not with manganese or nickel salts, and the metal is deposited when the intensity of the current has attained a certain minimum value which depends on the conc. of the soln. This phenomenon—*electrostenolysis*—was studied by

E. J. Mills, K. Söllner, H. Freundlich and K. Söllner, and A. Coehn and co-workers. Observations on the **thermoelectric force** of cobalt were made by T. J. Seebeck,<sup>25</sup> W. G. Hankel, E. Becquerel, A. Battelli, and P. G. Tait. K. Noll found the thermoelectric force of the *cobalt-platinum* couple to be -1.52 millivolts at 100°, where the negative sign means that the current at the cold junction flows from the platinum; G. Reichardt obtained -1.99 millivolts; and P. W. Bridgman,  $-1.679 \times 10^{-3}$  volt. Observations were also made by C. G. Knott and co-workers.

A. Schulze found that the thermoelectric force of the cobalt-platinum couple alters from 0° when  $E_0=0$  to 100° when  $E_{100}=-2.50$  millivolts. A minimum of -23.3 millivolts occurs at 960°. The temp. gradient,  $dE/d\theta$ , has a minimum at 350°, and a break between 465° and 470°. He observed:

	0°	100°	200°	350°	500°	600°	800°	1000°	1200°
$E_\theta$	0	-2.50	$\left\{ \begin{array}{l} \rightarrow 5.54 \\ \leftarrow 5.58 \end{array} \right.$	$\left\{ \begin{array}{l} -10.65 \\ -10.59 \end{array} \right.$	$\left\{ \begin{array}{l} -15.42 \\ -15.25 \end{array} \right.$	-17.99	-21.99	-23.19	-20.93
$\frac{dE}{dT}$		25.0	$\left\{ \begin{array}{l} \rightarrow -30.4 \\ \leftarrow -30.8 \end{array} \right.$	$\left\{ \begin{array}{l} -34.2 \\ -33.5 \end{array} \right.$	$\left\{ \begin{array}{l} -25.7 \\ -27.4 \end{array} \right.$	—	-16.5	-2.03	+14.6

The results in the vicinity of the temp. of magnetic transformation are plotted in Fig. 17, where  $E$  denotes the thermoelectric force in millivolts, and  $dE/d\theta$ , the temp. coeff. in millivolts per degree:

	1299°	1264°	1203°	1152°	1103°	1062°	1000.2°	904.3°	807.4°
$E$	-19.10	-19.73	-20.60	-21.27	-21.92	-22.46	-22.735	-22.64	-21.81
$dE/d\theta$		18.0	14.3	13.1	13.3	10.6	5.3	-0.96	-8.6

Observations were also made by W. Rohn, W. M. Latimer, and J. J. Schukoff. P. W. Bridgman gave  $-1.679 \times 10^{-3}$  volt for the thermoelectric force of cobalt against platinum with the cold junction at  $0^\circ$  and the hot junction at  $100^\circ$ . H. Péchaux found for the *cobalt-copper* couple :

	$0^\circ$	$100^\circ$	$200^\circ$	$300^\circ$	$400^\circ$	$500^\circ$	$600^\circ$	$700^\circ$	$800^\circ$	$900^\circ$
E.m.f. .	0.00	-2.32	-5.2	-8.6	-12.1	-17.8	-19.4	-22.9	-25.9	-28.4

G. Reichardt represented his results between  $50^\circ$  and  $200^\circ$  by  $E = 23.24\theta + 0.0413\theta^2$  microvolts ; for a hard-drawn wire between  $20^\circ$  and  $60^\circ$ ,  $E = 26.3$  microvolts, and after heating to dull redness, 25.8 microvolts. L. O. Grondahl and S. Karrer observed that with the cobalt-copper couple, the thermoelectric force decreases as the magnetic field increases in strength. P. McCorkle also observed a small increase as the value of  $dE/E$  in a longitudinal field, which attained a maximum at about 50 gauss, and the subsequent decrease attained a negative value at about 300 gauss. The effect of a small load was very small with strong magnetic fields. H. Péchaux, and C. Dannecker gave for the *cobalt-nickel* couple :—

	$0^\circ$	$100^\circ$	$200^\circ$	$300^\circ$	$400^\circ$	$500^\circ$	$600^\circ$	$700^\circ$	$800^\circ$	$900^\circ$
E.m.f. .	0.00	-0.3	-1.3	-2.6	-4.6	-6.9	-8.7	-9.8	-10.4	-10.1

With the cobalt-lead couple, the current goes from cobalt to lead through the hot junction, and G. Wietzel gave :

	$24.1^\circ$	$78.4^\circ$	$108.2^\circ$	$130.2^\circ$	$169.9^\circ$	$179.4^\circ$	$207.6^\circ$	$252.6^\circ$	$257.8^\circ$
$E$ .	-1.805	-1.860	-1.894	-1.888	-1.884	-1.440	-1.204	-1.491	-1.625

P. W. Bridgman gave for the cobalt-lead couple, e.m.f. =  $-17.32\theta - 0.390\theta^2$  microvolts between  $0^\circ$  and  $100^\circ$ . He also found that the thermal e.m.f.,  $E$ , microvolts or  $10^{-6}$  volt, of a couple composed of one branch of uncompressed metal, and the other, compressed by a press.  $p$  kgrms. per sq. cm. when the junctions are at  $0^\circ$  and  $\theta^\circ$  :

$p$	$10^\circ$	$20^\circ$	$40^\circ$	$60^\circ$	$80^\circ$	$100^\circ$
2,000 .	-0.29	-0.59	-1.22	-1.91	-2.65	-3.48
6,000 .	-0.86	-1.76	-3.69	-5.75	-7.92	-10.21
12,000 .	-1.72	-3.52	-7.34	-11.47	-15.90	-20.61

R. von Dallwitz-Wegner gave for the *cobalt-constantan* couple,  $-0.0009$  volt at  $100^\circ$ . W. H. Keesom and co-workers measured the thermoelectric force of the alloys against an alloy of gold and silver. O. L. Kowalke found for the thermocouples of *cobalt-nichrome*, the values indicated in (3), Fig. 18 ; for the *cobalt-advance* alloy (4), Fig. 18 ; for the *cobalt-constantan* (5), Fig. 18 ; for the *cobalt-iron* (2), Fig. 18 ; and for the *cobalt-nickel-iron alloy* (1), Fig. 18. J. Thiele studied the effect of the ageing of the metal on the thermoelectric force.

P. W. Bridgman found the **Peltier effect**,  $P$ , or the heat developed between compressed and uncompressed metal in joules per coulomb  $\times 10^6$  :

$P$	$0^\circ$	$20^\circ$	$40^\circ$	$60^\circ$	$80^\circ$	$100^\circ$
2,000 .	-7.6	-8.8	-10.3	-11.6	-13.8	-16.8
6,000 .	-22.7	-26.9	-31.3	-35.3	-39.5	-44.0
12,000 .	-45.9	-53.6	-62.2	-71.0	-80.3	-90.5

and for the cobalt-lead couple,  $P = (17.32 - 0.078\theta)(\theta + 273) \times 10^{-6}$  volts. P. W. Bridgman also found the **Thomson effect**,  $\sigma$ , or the heat excess in compressed and uncompressed metal in joules per coulomb  $\times 10^6$  :

$P$	$0^\circ$	$20^\circ$	$40^\circ$	$60^\circ$	$80^\circ$	$100^\circ$
2,000 .	-2.2	-2.9	-4.4	-6.7	-9.2	-13.8
6,000 .	-13.9	-12.6	-11.6	-11.3	-10.9	-10.4
12,000 .	-20.5	-22.0	-23.5	-25.0	-26.4	-28.0

and for the cobalt-lead couple,  $\sigma = -0.078(\theta + 273) \times 10^{-6}$  volts per degree. E. H. Hall, J. Monheim, and C. Benedicks discussed some theoretical phases of the subject.



E. H. Hall<sup>26</sup> found for the **Hall effect**—*vide* iron—with cobalt for  $H=3463$  gauss,  $R=2460 \times 10^{-6}$  at  $18^\circ$ ; for  $H=9000$  gauss,  $R=3550 \times 10^{-5}$  at  $19^\circ$ , and  $4440 \times 10^{-6}$  at  $48^\circ$ . A. von Ettinghausen and W. Nernst gave for  $H=5650$  gauss,  $R \times 10^6=1550$  at  $18^\circ$ . H. Zahn gave  $R \times 10^6=1010$  at  $18^\circ$ , and for  $H=4400$  gauss,  $R \times 10^6=1610$  at  $24^\circ$ . F. Unwin gave  $R \times 10^6=2450$  at  $18^\circ$ ; A. W. Smith,  $R \times 10^6=2400$  at  $24^\circ$  for  $H=17,000$  gauss; and H. B. Peacock gave  $R \times 10^6=29,000$  at  $18^\circ$ . A. Kundt studied the relation between the Hall effect and the magnetic field—*vide* iron; and H. B. Peacock, and A. J. Sorensen, the Hall effect with thin films. The Hall effect was also discussed by H. Tomlinson, and G. Borelius.

The **Corbino effect**—*vide* iron—was found by O. M. Corbino, A. K. Chapman, and E. P. Adams and A. K. Chapman to be 5.86 for cobalt, and the Hall effect 4.61 when referred to copper unity, the magnetic field being  $H=3560$ . For the **Ettinghausen effect**, *vide* iron. H. Zahn gave  $P \times 10^9=9$  at  $18^\circ$ , and 9 at  $24^\circ$  for  $H=4400$ ; F. Unwin, 21.6 at  $18^\circ$ ; and E. H. Hall, 81.0 at  $19^\circ$  for  $H=9000$  gauss; and 109.0 at  $48^\circ$  for  $H=9000$  gauss. For the **Nernst effect**—*vide* iron—H. Zahn found that  $Q \times 10^6=200$  at  $18^\circ$ ; F. Unwin, 780 at  $18^\circ$ ; A. von Ettinghausen and W. Nernst, 1540 at  $18^\circ$  when  $H=5650$  gauss; E. H. Hall, 1900 at  $25^\circ$  and 2190 at  $47^\circ$  for  $H=9000$  gauss; and A. W. Smith, 2000 at  $60^\circ$  for  $H=17,000$  gauss. For the **Leduc effect**—*vide* iron—H. Zahn gave  $S \times 10^9=130$  at  $18^\circ$ ; F. Unwin, 110 at  $18^\circ$ ; E. H. Hall, 377 at  $25^\circ$  and 429 at  $47^\circ$  for  $H=9000$  gauss; and A. W. Smith, 640 at  $53.7^\circ$  for  $H=11,800$  gauss. P. W. Bridgman discussed the relation between these thermomagnetic effects; J. Zahradnicel, the thermo-

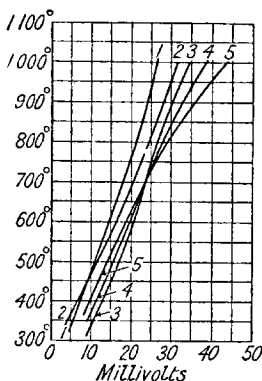


FIG. 18.—Thermoelectric Force of Thermocouples of Cobalt and Some Base Metals.

magnetic longitudinal effect; K. Honda, and J. R. Ashworth, the relation between the ferromagnetic constants and other properties; O. von Auwers, K. Honda, L. W. McKeehan, and W. Steinhaus, the relation between the ferromagnetic constants and the atomic or molecular structure; G. Borelius, the electron theory; P. Weiss, P. Weiss and O. Bloch, O. Bloch, W. Heisenberg, E. Stoner, K. Baedeker, L. L. Campbell, A. Carelli, W. W. Stiefler, J. Kunz, and A. Piccard, the magneton theory.

According to W. H. Wollaston,<sup>27</sup> cobalt is magnetic, so that its **magnetism** is to that of iron as 5 : 6 or 8 : 9; W. A. Lampadius said as 25 : 55. The subject was discussed by F. A. C. Gren, B. G. Sage, B. M. Tassaert, F. Kapf, R. Chevenix, T. J. Seebeck, J. J. Berzelius, J. C. Poggendorf, G. C. Haughton, C. B. Greiss, and B. Brodie. The metals here were not of a high degree of purity. M. Faraday said that the pure metal is not magnetic even at  $-80^\circ$ , but later added that it is magnetic. H. A. Rowland, and H. T. Kalmus and C. Harper added that purified cobalt is magnetic at all temp. up to about  $1150^\circ$ , at which temp., W. Guertler and G. Tammann found it to become non-magnetic. H. E. J. G. du Bois and O. Liebknecht added that the magnetic behaviour of cobalt is more like iron than is the case with nickel. This subject was studied by J. Thomsen, E. Wedekind, and E. van Aubel. The magnetic properties of cobalt were investigated by W. F. Barrett, A. Kundt, H. E. J. G. du Bois, W. Lobach, E. Becquerel, H. Becquerel, Lord Kelvin (W. Thomson), E. Maurer, E. H. Hall, D. Goldhammer, G. Fae, A. von Ettinghausen, W. Nernst, C. G. Knott and co-workers, P. Bachmetjeff, J. Plücker, W. G. Hankel, A. Gaiße, J. Trowbridge and A. L. McRae, T. Spooner, G. Berson, J. C. Beattie, G. Potapenko, T. Kahan, L. Néel, and H. N. Warren.

According to J. A. Ewing, cobalt has a greater capacity for magnetization than nickel, and under the influence of a strong field, it takes up as much magnetism as cast iron. Its magnetic susceptibility is small when the magnetizing force is weak.

The influence of the magnetic field,  $H$ , on the intensity of magnetization,  $I$ , on 93 per cent. cobalt, cast and annealed, was found by H. Nagaoka and K. Honda to be :

Cast	$\left\{ \begin{array}{l} H \\ I \end{array} \right.$	.	.	2.7	14.7	30.0	89.8	474	720
		.	.	3.0	274	467	778	1080	1136
Annealed	$\left\{ \begin{array}{l} H \\ I \end{array} \right.$	.	.	3.6	22.4	77.5	281	461	788
		.	.	4	38	188	439	568	699

Measurements were also made by H. Becquerel, J. A. Trowbridge and A. L. McRae, P. McCorkle, C. Asmus, R. Gans, M. Samuel, K. Honda, W. W. Stiefler, J. A. Ewing and W. Low, and H. Masumoto. H. T. Kalmus and K. B. Blake found for 99.6 per cent. cobalt :

$H$	.	.	2.5	20.7	43.2	75.9	129.0	151.8
$I$	.	.	8.5	136.7	238.4	350.2	451.5	493.2

H. E. J. G. du Bois gave for moderately strong fields, at  $100^\circ$  :

$H$	.	.	200	400	600	800	1000	1200
$I$	.	.	856	988	1032	1056	1080	1090

and K. Honda gave :

$H$	.	45.4	144	294	481	715	976	1257
$I$	.	529	737	882	972	1048	1098	1163

H. Masumoto found for the intensity of magnetization of cobalt :

$H$	.	5.3	10.6	26.0	51.2	101.6	207	421	637
$I$	.	8.4	14.6	61.8	155	347	547	750	878

S. Kaya observed that with crystals of cobalt,  $I$ , the intensity of magnetization is a maximum at  $26^\circ$ , so that for  $H=9000$  gauss,  $I=1422$ ; for an impure 93.1 per cent. cobalt. H. E. J. G. du Bois gave for  $H=8500$ ,  $I_{\max.}=1200$ ; and J. A. Ewing and W. Low, gave for cobalt with 1.66 per cent. of iron,  $H=15,000$ ,  $I_{\max.}=1310$ —a little greater than is the case with cast iron. For cobalt with 1.66 per cent. of iron, the magnetization constants were :

Magnetic force, $H$	.	.	.	1,350	4,040	8,930	14,990
Induction, $B$	.	.	.	16,000	18,870	23,890	30,210
Intensity of magnetization, $I$	.	.	.	1,260	1,280	1,290	1,310
Permeability, $\mu$	.	.	.	12.73	4.98	2.82	2.10

Under sufficiently strong magnetizing forces, less than 4000, the intensity of

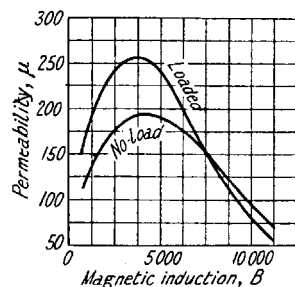


FIG. 19.—The Permeability of Cast Cobalt.

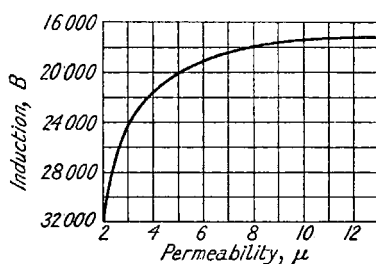


FIG. 20.—Permeability of Strongly-Magnetized Cobalt.

magnetization,  $I$ , reaches a constant or nearly constant value. In stronger fields, the relation  $B=16,300+H$  exists. The results are summarized in Fig. 19. O. Bloch found for a field of 10,000 gauss, the saturation values  $B-H=4\pi I_\infty$  :

	- 273°	181°	409°	545°	781°	926°	1040°	1115°
$4\pi I_\infty$	(170.20)	166.32	159.40	151.30	131.85	109.20	78.55	27.13

—vide the cobalt-nickel alloys, Fig. 20. H. T. Kalmus and K. B. Blake measured  $BH$ -curves for purified cobalt; R. Gans, and M. Samuel, the permeability. P. Weiss found that the law of approach of cobalt to the saturation value of the

intensity of magnetization,  $\sigma$ —i.e. the intensity of magnetization per gram—is  $\sigma = 162(1 - 1.11 \times 10^6 H^{-2})$ , and at  $17^\circ$ , the saturation value  $\sigma = 162$ . This was confirmed by A. Droz; whilst P. Weiss and H. K. Onnes obtained  $\sigma = < 163.6$  at the temp. of liquid hydrogen. W. W. Stiefler observed that the saturation value  $\sigma_\infty$  is a function of the temp., so that:

	22°	235°	414°	698°	991°	1065°	1104°	1152°
$\sigma_\infty$	161.0	154.0	146.4	125.2	73.3	30.0	2.2	?

and further:

	22°			235°			414°		
H	725	3450	4270	625	3026	4386	460	3135	4515
$\sigma$	102.4	153.2	155.2	108.4	151.8	152.8	119.2	146.3	146.4

	874°			1065°			1104°		
H	215	2015	3915	1165	3060	4010	1400	2400	3050
$\sigma$	83.4	97.9	97.9	21.4	30.0	29.4	1.3	1.9	2.6

Measurements of the saturation were also made by R. I. Allen and F. W. Constant, P. Weiss, P. Weiss and R. Forrer, P. Weiss and H. K. Onnes, L. W. McKeehan, A. J. Sorensen, A. Droz, M. Samuel, F. Bloch, O. Bloch, A. Preuss, R. Sanger, and F. C. Powell. M. J. O. Strutt studied the magnetization of cobalt in fields of high frequency.

S. Kaya prepared large single crystals of cobalt and cut discs through the (0001)- and (1010)-planes respectively—Fig. 21. Magnetization was easy in the (1010)-plane in the direction

of (0001), but difficult in the direction (1010). The permeabilities in the two directions were respectively 380, and 4. The parallel and perpendicular components of the magnetization vary with a period of  $180^\circ$

in this plane. In the (0001)-plane, magnetization was difficult in the directions of both the principal axes (1010) and (1120). The saturation value for a single crystal rod, with its axes parallel to the direction of easy magnetization, (0001), was 1422 at  $26^\circ$ . It is suggested that the results are explained by the theory of K. Honda and Y. Okubo. K. Honda and H. Masumoto measured the magnetization of single crystals of cobalt, and some results are summarized in Fig. 22. The direction of the (0001)-axes is that of easy magnetization, and as the temp. is raised, the magnetization in weak fields increases up to  $230^\circ$  and then decreases. The saturation value for the magnetization of cobalt at absolute zero is estimated to be 1446 c.g.s. units. The directions of the (1010)- and (1120)-axes

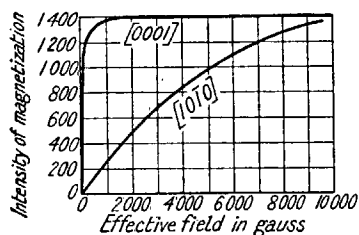


FIG. 21.—Magnetization of Single Crystals of Cobalt.

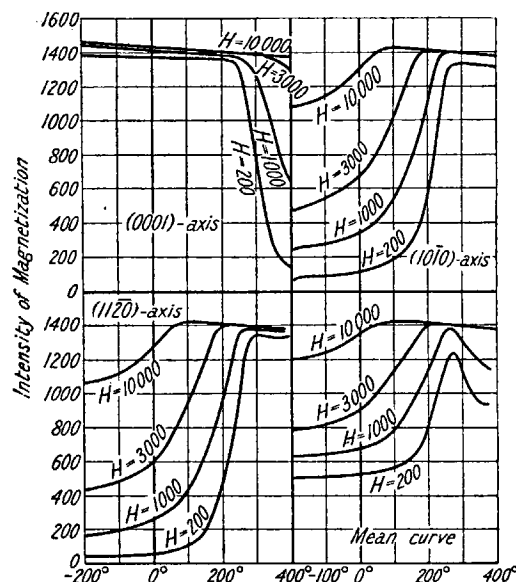


FIG. 22.—The Magnetization of Single Crystals of Cobalt.

are those of difficult magnetization. With a rise of temp. the magnetization increases up to  $300^\circ$ , and then remains almost constant. F. Bitter made some

observations with single crystals. F. C. Powell, and N. S. Akuloff studied the magnetic properties of single crystals of cobalt; and J. D. Hanawalt and L. R. Ingersoll, E. P. T. Tyndall and W. W. Wertzbaugher, L. C. Jackson, and A. J. Sorensen, the magnetic properties of thin films of cobalt; and H. E. Malmstrom observed no ageing effect. F. Bloch and G. Gentile, O. Dahl and J. Pfaffenberger, and N. S. Akuloff investigated the magnetic anisotropy of cobalt.

H. A. Rowland found a maximum susceptibility of 11.2. The rounded curves for cobalt resemble those for hardened iron. The residual magnetism is comparatively small, and the coercive force is 12. E. Maurer observed that cold-worked cobalt, annealed at different temp., gives a maximum induction  $B$ , and a maximum remanence, when annealed at 700°:

Annealed at . . .	20°	100°	300°	500°	650°	700°	750°	900°
Induction . . .	8,000	7,800	7,500	8,950	11,000	13,000	12,950	10,650
Remanence . . .	2,950	2,900	2,825	3,275	4,050	5,025	4,675	3,376
Coercive force . .	55.2	56.0	59.0	45.0	26.2	15.2	13.5	17.6

G. Berson measured the residual magnetism in cast cobalt, and found that, like the intensity of magnetization, with a constant field, it rises about 2.5 times as the temp. passes from 20° to 320°; and J. R. Ashworth calculated the ratio of the remanent magnetism at  $\theta^\circ$  to its value at  $-273^\circ$ , to be:

	14°	20.9°	300°	390°	472°	560°	747°
Ratio . . . . .	0.985	0.975	0.974	0.933	0.910	0.877	0.786

Observations were made by A. Perrier, and C. Asmus found that the maximum induction and remanence of cobalt increases with the magnitude of the step-by-step magnetization of the metal. The coercive force remains virtually unchanged. The coercive force of cobalt was measured by R. Gans. The results of M. Samuel are summarized in Fig. 23 for two different samples of cobalt. A. Kussmann

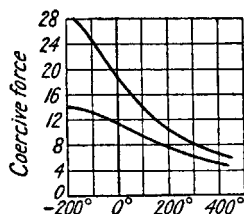


FIG. 23.—The Coercive Force of Cobalt at Different Temperatures.

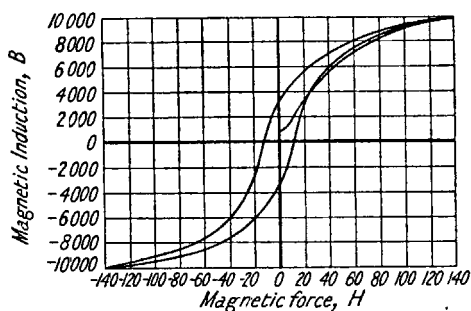


FIG. 24.—The Cyclic Magnetization of Cobalt.

and B. Scharnoff discussed the relation between the coercive force and the mechanical hardness; and W. Luthe, and C. Asmus, the magnetic viscosity.

In the cyclic magnetization of a cast and turned cobalt rod with about 2 per cent. of iron, Fig. 24, J. A. Ewing observed a small initial magnetism; the greatest permeability, 174, occurred when the force was about 25, and this corresponded with a magnetic susceptibility of about 13.8. J. A. Fleming and co-workers observed that with 95.95 per cent. cobalt, the maximum values of the induction,  $B$ , field-strength,  $H$ , and the hysteresis loss, in ergs per sq. cm., were:

$H$ . . . . .	6.67	25.76	48.54	75.46	114.03
$B$ . . . . .	911	4110	5869	7052	8237
Hysteresis loss. . . .	452	160	121	93	72

corresponding with: Hysteresis loss =  $0.01B^{1.6}$  ergs per sq. cm. Observations were made by C. P. Steinmetz, W. Elenbaas, M. Samuel, W. W. Stiefler, R. Forrer and J. Martek, H. T. Kalmus and K. B. Blake, and H. E. J. G. du Bois. R. Beattie

observed a maximum hysteresis loss for an intensity of magnetization 700. K. Honda and S. Shimizu measured the hysteresis losses with cast cobalt, and the same metal annealed at 1100°, at ordinary temp., say 20°, and at -186°, and found :

	Cast Cobalt				Annealed Cobalt			
	20°		-186°		20°		-186°	
$H$	6.6	92.4	7.4	96.3	43.7	218.0	48.3	224.3
$B$	1,107	9,259	960	8,676	1,802	5,508	1,115	4,446
Loss	481	21,220	441	22,880	5,669	35,770	3,244	38,710

The Barchausen effect—*vide* iron—was studied by R. F. de Waard.

The effect of temperature on the magnetization of cobalt was studied by E. Becquerel, M. Faraday, G. Berson, R. Forrer, and H. E. J. G. du Bois. The temp. coeff. of magnetization was found by J. R. Ashworth to be 0.0005 between 0° and 100°, and 0.00015 between 100° and 200°.

With annealed cobalt, K. Honda, K. Honda and S. Shimizu found that the variation of the magnetization curve with temp. has two maxima and two minima,

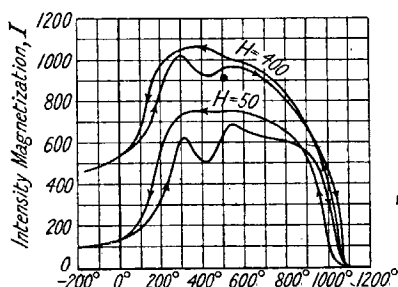


FIG. 25.—The Effect of Temperature on the Magnetization of Cobalt.

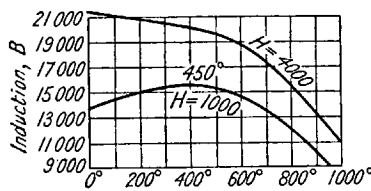


FIG. 26.—The Effect of Temperature on the Magnetic Induction of Cobalt.

Fig. 25. They found the intensity of magnetization,  $I$ , of cast cobalt, with different field-strengths,  $H$ , to be :

-186°	$\left\{ \begin{array}{l} H \\ I \end{array} \right.$	$\left\{ \begin{array}{l} 3.90 \\ 28 \end{array} \right.$	$\left\{ \begin{array}{l} 10.57 \\ 122 \end{array} \right.$	$\left\{ \begin{array}{l} 39.3 \\ 427 \end{array} \right.$	$\left\{ \begin{array}{l} 206.9 \\ 848 \end{array} \right.$	$\left\{ \begin{array}{l} 449 \\ 999 \end{array} \right.$	$\left\{ \begin{array}{l} 668 \\ 1063 \end{array} \right.$
20°	$\left\{ \begin{array}{l} H \\ I \end{array} \right.$	$\left\{ \begin{array}{l} 5.1 \\ 72 \end{array} \right.$	$\left\{ \begin{array}{l} 10.7 \\ 170 \end{array} \right.$	$\left\{ \begin{array}{l} 35.7 \\ 497 \end{array} \right.$	$\left\{ \begin{array}{l} 147.7 \\ 865 \end{array} \right.$	$\left\{ \begin{array}{l} 392 \\ 1027 \end{array} \right.$	$\left\{ \begin{array}{l} 610 \\ 1088 \end{array} \right.$

and similarly, for annealed cobalt :

-186°	$\left\{ \begin{array}{l} H \\ I \end{array} \right.$	$\left\{ \begin{array}{l} 7.80 \\ 9 \end{array} \right.$	$\left\{ \begin{array}{l} 39.0 \\ 64 \end{array} \right.$	$\left\{ \begin{array}{l} 80.0 \\ 148 \end{array} \right.$	$\left\{ \begin{array}{l} 167.4 \\ 282 \end{array} \right.$	$\left\{ \begin{array}{l} 347 \\ 426 \end{array} \right.$	$\left\{ \begin{array}{l} 702 \\ 589 \end{array} \right.$
31°	$\left\{ \begin{array}{l} H \\ I \end{array} \right.$	$\left\{ \begin{array}{l} 4.94 \\ 8 \end{array} \right.$	$\left\{ \begin{array}{l} 29.23 \\ 56 \end{array} \right.$	$\left\{ \begin{array}{l} 65.0 \\ 164 \end{array} \right.$	$\left\{ \begin{array}{l} 147.5 \\ 313 \end{array} \right.$	$\left\{ \begin{array}{l} 484 \\ 572 \end{array} \right.$	$\left\{ \begin{array}{l} 684 \\ 664 \end{array} \right.$
185°	$\left\{ \begin{array}{l} H \\ I \end{array} \right.$	$\left\{ \begin{array}{l} 13.45 \\ 49 \end{array} \right.$	$\left\{ \begin{array}{l} 19.52 \\ 96 \end{array} \right.$	$\left\{ \begin{array}{l} 63.5 \\ 325 \end{array} \right.$	$\left\{ \begin{array}{l} 94.3 \\ 411 \end{array} \right.$	$\left\{ \begin{array}{l} 279.2 \\ 677 \end{array} \right.$	$\left\{ \begin{array}{l} 376 \\ 758 \end{array} \right.$
619°	$\left\{ \begin{array}{l} H \\ I \end{array} \right.$	$\left\{ \begin{array}{l} 2.48 \\ 32 \end{array} \right.$	$\left\{ \begin{array}{l} 4.79 \\ 108 \end{array} \right.$	$\left\{ \begin{array}{l} 31.31 \\ 573 \end{array} \right.$	$\left\{ \begin{array}{l} 72.1 \\ 716 \end{array} \right.$	$\left\{ \begin{array}{l} 128.5 \\ 806 \end{array} \right.$	$\left\{ \begin{array}{l} 378 \\ 951 \end{array} \right.$
1060°	$\left\{ \begin{array}{l} H \\ I \end{array} \right.$	$\left\{ \begin{array}{l} 4.14 \\ 56 \end{array} \right.$	$\left\{ \begin{array}{l} 22.03 \\ 84 \end{array} \right.$	$\left\{ \begin{array}{l} 51.1 \\ 98 \end{array} \right.$	$\left\{ \begin{array}{l} 212.5 \\ 126 \end{array} \right.$	$\left\{ \begin{array}{l} 333 \\ 136 \end{array} \right.$	$\left\{ \begin{array}{l} 439 \\ 140 \end{array} \right.$

H. Wilde found that the variation in magnetization of cobalt in a weak magnetic field rises at first, gradually reaches a maximum at about 400°, and then decreases slowly, to vanish at the critical temp. This was confirmed by H. Nagaoka and S. Kusakabe, R. Ruer and co-workers, K. Honda and S. Shimizu, and H. Masumoto, who obtained the curves shown in Fig. 25, where in a field of 1000 gauss the magnetic induction increases gradually with rise of temp., and after passing through a maximum at 450°, decreases slowly. H. Wilde found that in strong fields, say

1000 gauss, the magnetization of cobalt decreases gradually from the beginning without showing any maximum—Fig. 26. If  $\sigma$  denotes the intensity of magnetization per gram, A. Preuss gave for  $H=10,000$  gauss :

	17°	510°	693°	844°	971°	1090°	1133°	1144°	1149°
$\sigma$	165.5	149.2	136.9	120.5	99.37	62.53	32.09	20.64	17.89

Observations were also made by O. Bloch, H. Masumoto, W. W. Stiefler, and F. Tyler. O. Bloch gave for the magnetic susceptibility,  $\chi$  :

	951°	984°	1027°	1084°	1146°	1151°	1245°
$\chi \times 10^6$	9.90	9.56	9.07	8.54	7.92	7.85	7.16

and P. Weiss and G. Foex :

	1156°	1170°	1188°	1208°	1241°	1242°	1261°	1260°	1302°
$\chi \times 10^{-6}$	785.3	560.2	384.4	283.1	197.3	196.1	162.7	139.8	119.1

Observations were also made by A. Preuss, and E. M. Terry.

P. Weiss and G. Foex said that Curie's law— $C=\chi(T-\theta)$ , where  $C$  is Curie's constant, and  $\theta$  the transformation temp. on the absolute scale—holds for  $\beta$ -iron- $\beta$ -nickel, and  $\beta$ -cobalt at low temp., and that the points for the reciprocal susceptibility and temp. lie not on a straight line but rather on two straight lines which intersect at 1241°, and they accordingly speak of the  $\beta_1$ - and  $\beta_2$ -states. E. M. Terry could not confirm this. His data for cobalt are plotted in Fig. 27. When plotted on a larger scale, starting from the transformation point, 1100°, the curve for the reciprocal susceptibility has a gradual upward curvature throughout the entire region up to the m.p., 1485°; at this temp. there is a slight break in the susceptibility curve. These results do not agree with those of P. Weiss and G. Foex, and Curie constants for the metals cannot be deduced.

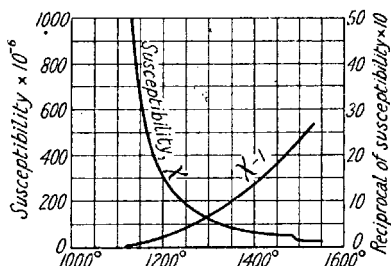


FIG. 27.—The Effect of Temperature on the Magnetic Susceptibility of Cobalt.

M. Faraday observed that the critical temp. of cobalt, that is, the temp. at which it loses its ferromagnetic properties, is near 1083°, the m.p. of copper, and analogous observations were also made by C. S. M. Pouillet, H. Wilde, and E. Becquerel. J. Pionchon added that some ferromagnetism is lost even at 300°, and almost all at about 900°; and H. Nagaoka and K. Honda observed that some is lost at 450°, and almost all at 1090°. The temp. of magnetic transformation, or the Curie point, that is, the temp. at which cobalt passes from the ferromagnetic to the paramagnetic state, was found by W. Guertler and G. Tammann to be 1150°, and later, they gave 1143° on a heating curve, and 1145° on a cooling curve; U. Raydt and G. Tammann gave 1143°; S. Umino, 1050°; R. Sahmen, 1115°; A. Schulze, 1128°; H. Nagaoka and S. Kusakabe, 1100°; K. Honda and S. Shimizu, 1090°; K. Honda, 1140°; K. Lewkonja, 1134°; W. W. Stiefler, 1075°; H. Masumoto, 1115°; P. Weiss, 1100°; O. Bloch, 1121° for  $H=10,000$  gauss, and 1115° for  $H=\sigma$ ; A. Göbl, 1112°; R. Ruer and K. Kaneko, 1112°; F. Wüst and co-workers, 950° to 1100°; and F. Wever and U. Haschimoto, 1115° to 1128°. The temp. of magnetic transformation corresponds with the  $A_2$ -arrest of iron at 790°, and of nickel at 380°. J. J. Schukoff observed a small evolution of heat occurs on the cooling curve of cobalt at about 985°; and K. Honda noted that the phenomenon is much smaller with annealed cobalt than it is with the cast metal. F. Wüst and co-workers calculated for the sp. ht. a heat of transformation of 14.70 cal. per gram at 1025°, but other observers obtained higher values for the sp. ht. than did F. Wüst and co-workers. S. Umino obtained a heat absorption

of 2.0 cal. per gram with two kinds of cobalt at 1150°. The Curie point was studied by R. Ruer and K. Bode, and by R. Forrer—*vide* iron.

C. S. Yeh measured the effect of hydrostatic pressure on the magnetization of cobalt, and obtained the results plotted in Fig. 28. The values of  $dB/B_0$  are expressed in percentages per 1000 kgrms. per sq. cm. :

$H$	.	.	.	10.9	21.8	32.8	45.2	56.1	72.4	79.5
$B$	.	.	.	380	981	1562	2130	2580	3165	3420
$dB/B_0$	.	.	.	-0.2	-0.2	+0.09	+0.27	+0.25	+0.38	+0.41

The press. coeff. of magnetization per unit vol.  $\sigma B/B_0$  is expressed in per cent. per 1000 kgrms. per sq. cm.; it is negative for fields below 30 gauss, but positive for higher fields.

J. A. Ewing and W. Low measured the permeability of cobalt under no stress, and then under a series of loads producing compressive stress, and some results in Fig. 29 show the curves for no load, and for a load of 16.2 kgrms. per sq.

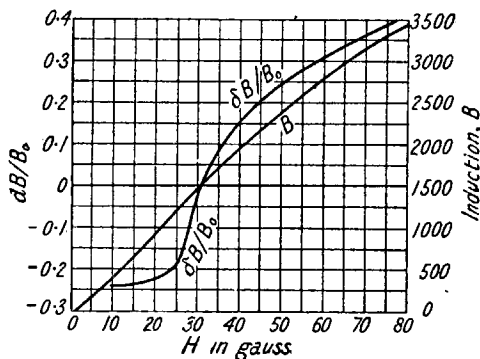


FIG. 28.—The Effect of Pressure on the Magnetization of Cobalt at 20°.

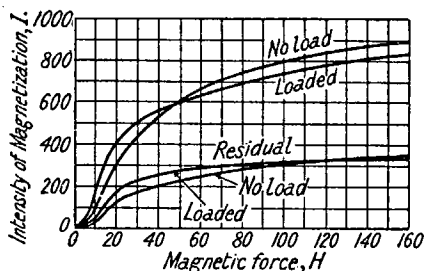


FIG. 29.—Induced and Residual Magnetism of Cobalt with and without Compressive Load.

mm. cross-section. Thus, under weak magnetic forces, the permeability of cobalt is increased by compressive stress, but when the magnetic force is large, the reverse is the case. C. Chree also obtained a reversal by pressure. The reversal also occurs with iron. H. Tomlinson studied the Villari critical temp. where traction produces no change in magnetic permeability; and J. W. Peck and R. A. Houston, the relations between stress and magnetization. The effect of press. was discussed by H. Nagaoka and K. Honda, P. McCorkle, and G. Wiedemann.

Lord Kelvin found that pulling decreased and relaxing the pull increased the induced magnetism of a cobalt bar hung vertically in the earth's magnetic field. C. Chree found that a reversal, resembling the Villari reversal of iron but opposite in character, occurs for longitudinal pressure, increases the magnetism in weak fields, but reduces it in strong fields. J. A. Ewing's curves, Fig. 29, illustrate the effect with a stress of 16.2 kgrms. per sq. mm. The crossing of the curves correspond with the reversal observed by C. Chree. There is also a reversal with the curves of residual magnetism with heavier loads. S. Bidwell found that the magnetic contraction of cobalt wires is not materially affected by tension.

W. F. Barrett observed that when cobalt is placed in a magnetic field, it increases in length, but C. Asmus found the decrease in length indicated in Fig. 30 to be produced by the magnetization of ordinary and annealed cobalt. The change is represented as a decrease in length in ten-millionths of the original length of the rod. The results obtained by K. Honda and S. Shimizu are indicated in Fig. 31, where the ordinate represents the change of magnetic expansion, and the abscissa, the temp. Each of the three curves for fields of  $H=100, 400$ , and  $900$  gauss, passes through the same point  $460^\circ$ , showing that cobalt undergoes a reversible magnetic

expansion above and below  $460^\circ$  for all field-strengths. H. Masumoto said that the rearrangement of the atoms affects the magnetization in a weak field but not

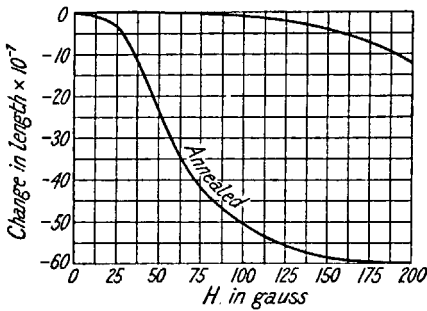


FIG. 30.—Deformation produced by the Magnetization of Cobalt.

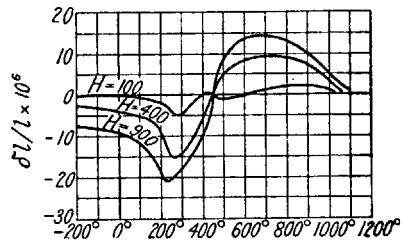


FIG. 31.—The Effect of Temperature on the Expansion of Cobalt in Magnetic Fields of different Strengths.

in a very strong field where all the elementary magnets take the direction of the field. Consequently, the magnetization curves of cobalt before and after the transformation coincide in a strong field, so that the transformation appears only in the magnetization in a weak field, but vanishes in that of a strong field. S. Bidwell found that the changes in length with cobalt are almost but not quite independent of the presence of a longitudinal tensile stress. The subject was studied by A. Schulze. K. Honda and S. Shimizu's observations on the effect of temp. and magnetizing force on the magnetostriction of cast and annealed cobalt are summarized in Fig. 32. H. Masumoto gave for the magnetostriction of cobalt:

$H$	18.6	60.1	120.1	182	308	498	625
$\delta l/l \times 10^6$	-0.10	-0.34	-1.24	-2.34	-4.33	-7.13	-9.08

and K. Honda and K. Kido:

$H$	26.0	52.1	106.3	181.8	376.7	574.6
$\delta l/l \times 10^6$	-0.94	-2.61	-4.72	-6.68	-8.84	-10.41

Z. Nishiyama found that with single crystals in the direction of the axis of the hexagonal lattice, that is, of easy magnetization, there are small longitudinal and transverse contractions, Fig. 33. When the magnetic field is applied in a direction perpendicular to the axis, that is, in the direction where magnetization is difficult, the longitudinal effect is negative, and in the direction parallel to the base, the transverse effect is also negative, but positive in the direction of the axis. The magnitude of these effects is great when compared with the effect obtained when the magnetic field is applied in the direction of the hexagonal lattice. When the field is applied in the intermediate direction, the magnetostriction is rather larger than that in the principal directions. S. Kaya, S. R. Williams, H. Masumoto, A. Schulze, Y. Masiyama, W. Fricke, C. Asmus, H. A. Pigeon, R. Becker and M. Kornetzky, and P. McCorkle studied the subject.

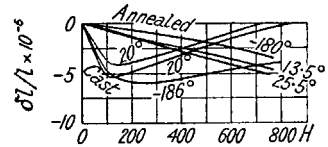


FIG. 32.—The Effect of Temperature and Magnetizing Force on Magnetostriction of Cast and Annealed Cobalt.

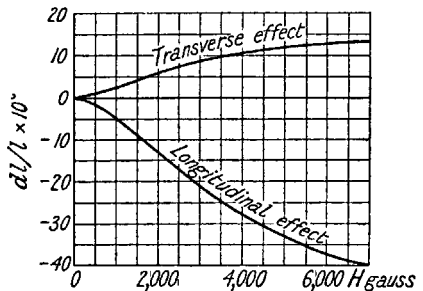


FIG. 33.—The Changes in Length and Width by Magnetization.



G. Wiedemann discovered that when iron was suspended in a very small, vertical magnetic field, while at the same time an electric current flowed through the specimen, its free end was observed to twist in such a direction that to an observer looking along the specimen in the direction of the flow of current and also in the direction of the magnetic lines of force, the lines of twist were in the direction of a

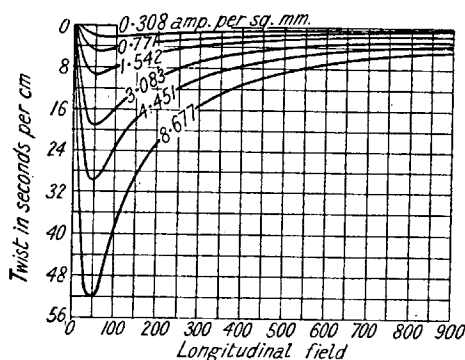


FIG. 34.—The Magnetostriction in the Circular Magnetization of Cobalt.

right-handed screw, that is, the twist was positive in direction. The direction of twist was reversed upon the reversal of either the current or the longitudinal field. If the current in the specimen remained constant and the longitudinal field was gradually increased, the twist reached a maximum in fields of from 15 to 36 gauss, gradually decreased in stronger fields until in very strong fields the direction of twist changed and became negative or left-handed. This is commonly known as the *Wiedemann effect*. Observations on the effect with cobalt were made by C. G. Knott, and the results with the

circular magnetization of cobalt with currents from 0.308 to 6.677 amp. per sq. mm., by H. A. Pigeon, are summarized in Fig. 34, and the subject was discussed by K. Honda and S. Shimizu, H. A. Pigeon, and P. McCorkle. The gyromagnetic effect—*vide* iron—was studied by W. Sucksmith, D. M. Bose, D. M. Bose and H. G. Bhar, J. Dorfmann, and R. Jaanus and K. Honda; magnetization by rotation, by S. J. Barnett, S. J. and L. J. H. Barnett, and K. Honda; W. Köster and W. Schmidt, the lattice parameter and ferromagnetism; and the effect of a magnetic field on the viscosity, by E. Drago.

J. R. Ashworth studied the relation between the thermal and magnetic constants of cobalt. K. Honda and T. Tanaka observed that, unlike the case with iron, the elastic constants of cobalt are reduced by magnetization for all fields; they obtained for the effect of magnetization on the elastic modulus,  $E$ , and the coeff. of rigidity,  $K$ , the following values:

$H$	10.5	33.1	75.2	108	180	287	442
$\delta E/E \times 10^2$	0	-0.25	-0.45	-0.50	-0.50	-0.50	-0.55
$H$	22.5	55.0	111.0	160	257	325	402
$\delta K/K \times 10^2$	-0.045	-0.123	-0.160	-0.160	-0.180	-0.190	-0.200

P. Weiss and co-workers found the magnetic moment to be 8.67 for  $\gamma$ -cobalt, and 9.0 for cobalt alloyed with nickel; and P. Weiss and R. Forrer gave 9 and 17 for the atomic moment of  $\alpha$ -cobalt. W. W. Stiefler calculated for the intrinsic molecular field,  $H_m=8,870,000$ ; for the moment of the elementary magnet,  $M=6.21 \times 10^{-20}$ ; for the number of atoms in an elementary magnet,  $n=4$ ; and for the elementary charge,  $e=4.65 \times 10^{-10}$  electrostatic units. The subject was discussed by C. Sadron, A. Chantillon, L. C. Jackson, A. Serres, P. Weiss and co-workers, S. Datta, K. R. More, E. C. Stoner, and H. Vatter. The position of cobalt in the theory of ferromagnetism was discussed by J. Dorfmann and R. Jaanus, A. Wolf, H. Fahlenbrach, R. Forrer, P. Collet, W. Heisenberg, E. C. Stoner, P. S. Epstein, I. Tamm, J. C. Slater, W. J. de Haas and E. C. Wiersma, H. Sachsse, G. Foëx, and F. Tyler—*vide* iron. E. H. Williams discussed the possibility that chemical bonds are formed by magnetic forces.

S. S. Bhatnagar and co-workers found that cobalt salts lose their paramagnetism and become diamagnetic when adsorbed on charcoal, and this is thought to favour the view that the adsorption is a case of chemical combination. The subject was

discussed by D. M. Bose and co-workers. I. I. Rabi, J. H. van Vleck, R. W. Roberts, B. Cabrera, W. Klemm and co-workers, P. C. Ray and H. Bahr, R. Schlapp and W. G. Penney, L. A. Welo, R. Mercier, P. Collet, R. Gans and E. Czerlinsky, and L. Cambi and L. Szegő. H. A. Rowland and L. Bell studied the action of a magnetic field while cobalt is being attacked by chemical reagents; and D. M. Bose and P. K. Raha, the photo-magnetic effect with cobaltous salts.

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### § 7. The Chemical Properties of Cobalt

W. Ramsay and J. N. Collie<sup>1</sup> found that **helium** has no chemical action on cobalt, at a red-heat; and when cobalt electrodes are spluttered in liquid **argon**, F. Fischer and F. Schröter observed no chemical action.

According to R. C. Böttger,<sup>2</sup> a thin strip of cobalt can adsorb **hydrogen**. G. P. Baxter found that cobalt in the form of ingots occludes very little hydrogen, but when reduced from its oxides, in hydrogen, so that the metal is in a fine state of subdivision, it occludes relatively large amounts of this gas. The vol. of occluded hydrogen varies, in the case of metal reduced from the oxide, with its purity and the temp. of reduction; it is remarkable that the metal reduced from cobalt bromide occludes practically no hydrogen; this appears to be due to its being deposited in a more compact form than that reduced from the oxide, as the presence of sodium bromide has no perceptible effect on the amount of occluded gas. Since the occlusion of hydrogen progresses very slowly at the ordinary temp. and is practically negligible at the temp. of reduction (400° to 500°), it must be a maximum at some intermediate temp.; the time during which the metal is in contact with hydrogen determines largely the amount of gas taken up. Although practically none of the hydrogen occluded is given off in vacuo at the ordinary temp., yet on heating in vacuo nearly the whole is evolved. L. J. Troost and P. Hautefeuille said that the metal reduced at 400° occludes about 100 times its vol. of hydrogen and this gas is given off on heating the metal in vacuo at 200°. G. Neumann and F. Streintz found that the metal can occlude 153 vols. of the gas, and if the experiment is repeated a number of times, 59-31 vols. are occluded. Observations were also made by T. W. Richards and co-workers, N. I. Nitikin, W. Hempel and H. Thiele, and H. Copaux. According to A. Sieverts and co-workers, the adsorption is measurable at 700°, and 760 mm.:

	700°	800°	900°	1000°
Hydrogen	0.17	0.25	0.34	0.52 c.c. occluded

M. M. Raessler observed that under similar conditions the hydrogen occluded by electrolytic cobalt is less than that by iron, and greater than that by nickel. It decreases with increasing thickness, and temp., but it increases with increasing

acidity of the electrolyte. H. S. Taylor and R. M. Burns found that between 25° and 218°, 1 vol. of cobalt absorbs less than 0.05 vol. of hydrogen. The hydrogen is given off at 400°, and the metal is readily oxidized. G. Neumann and F. Streintz observed that the repeated oxidation and reduction decreases the power of cobalt to occlude hydrogen, owing, said G. P. Baxter, to the increasing compactness of the metal. A. Sieverts represented the effect of pressure,  $p$ , on the solubility,  $S$ , of hydrogen in cobalt, by  $S = k\sqrt{p}$ , where  $k$  is a constant. N. I. Nitikin also made observations on this subject; and N. I. Nitikin, and D. Alexejeff and L. Savinina studied the diffusion of hydrogen in cobalt. The presence of impurities has no perceptible influence on the power of cobalt to occlude hydrogen. Observations were made by C. J. Smithells. B. Neumann also studied the absorption of hydrogen by cobalt salts; and R. Hocart, A. E. Mitchell and A. L. Marshall, A. Kailan and J. Kohberger, G. F. Hüttig and R. Kassler, R. Schenck and H. Klas, C. M. Loane, H. W. Underwood, H. Remy, W. P. Yant and C. O. Hawk, A. Kailan and O. Stüber, P. Sabatier, P. Sabatier and J. B. Senderens, and O. Schmidt, the catalytic action of cobalt in the hydrogenation of organic compounds, etc. T. Weichselfelder and B. Thiede found that when cobaltous chloride is treated with magnesium phenyl bromide in an atm. of hydrogen, **cobalt dihydride**,  $\text{CoH}_2$ , is formed. F. Gläser reduced cobalt oxide in hydrogen and found that at 250°, the results corresponded with  $\text{CoH}_3$ , and at 306°, with  $\text{CoH}_2$ . H. Copaux also reported the formation of the hydride, but A. Sieverts did not accept the evidence. G. Hägg studied the mol. vol. of the hydride; and G. F. Hüttig and co-workers, their relations with other hydrides.

According to J. J. Berzelius,<sup>3</sup> and H. V. Regnault, compact cobalt does not oxidize in **air** at ordinary temp., but it becomes superficially oxidized at a red-heat; and at an intense heat, the metal burns with a red-light. C. F. Schönbein added that the cold metal, which has been heated to the temp. of oxidation, contains a thin film of higher oxides. J. Jahn found that with cobalt at :

	Moist Air		Dry Air	
	199°	300°	198°	297°
Cobalt . . . . .	3940.3	3939.4	2975.2	2971.1 mgrms.
Gain in weight . . .	0	0.3	0	0.2

N. B. Pilling and R. E. Bedworth studied the oxidation of cobalt heated in air, and found the critical density ratio to be 2.10, whereas with copper the value was 1.70, and with iron, 2.07—*vide* iron. The subject was also discussed by G. Tammann and co-workers. H. P. Walmsley examined the nature of the smoke obtained by burning cobalt in air between electrodes of cobalt. G. Magnus observed that when reduced from the oxide at a low temp., cobalt is pyrophoric, and H. Hess added that the metal powder reduced at a red-heat, gradually forms the oxide on exposure to air. H. Moissan noted that the metal powder obtained by distilling the amalgam at 350° is not pyrophoric, but that the metal obtained by reducing the oxide in hydrogen at 250° is pyrophoric. The metal charged with occluded hydrogen was found by W. C. Henry to turn red-hot in a jet of **oxygen**. R. Schenck and H. Wesseldonk found that cobalt is activated towards oxygen by heating the finely-divided metal with oxides of those metals which form solid soln. or chemical compounds with cobalt oxide—*e.g.*,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{MnO}$ , and  $\text{Al}_2\text{O}_3$ . W. Biltz and W. Holverscheid found that the powdered metal can be preserved in a closed vessel, since on exposure it acquires a thin, protective film of oxide; but when very finely-divided, A. Krause observed that the metal is oxidized rather more quickly than nickel—*vide supra*, pyrophoric cobalt. H. W. Underwood studied cobalt as a catalyst in oxidation processes. Red-hot cobalt was found by H. V. Regnault, C. M. Despretz, and J. Thomsen to decompose **water** vapour; but, as shown by J. J. Berzelius, the metal is not attacked by water at ordinary temp. G. Chaudron found that in the reaction:  $\text{Co} + \text{H}_2\text{O} \rightleftharpoons \text{CoO} + \text{H}_2$ , the press. of water vapour at 800° is 10.9 mm.,

and of hydrogen, 0.3 mm.; at 1000°, 9.65 and 0.46 mm.; and at 1050°, 9.6 and 0.42 mm. W. Guertler and T. Liepus observed that cobalt is attacked during 8 hrs'. exposure to sea-water, sea-water plus air, and rain-water plus air. S. S. Bhatnagar and S. L. Bhatia studied the rate of evaporation of adsorbed water from cobalt; N. M. Zarubin, the rate of settling in water. H. Remy, and H. Remy and H. Gönning discussed the catalytic action of cobalt on detonating gas. W. Merckens observed that some hydrogen dioxide is formed when cobalt oxidizes in moist air. C. F. Schönbein noted that **hydrogen dioxide** is readily decomposed when in contact with cobalt, or cobalt salts, and the reaction was studied by A. Quartaroli, S. F. Cook, and A. C. Robertson.

H. Davy<sup>4</sup> observed that heated cobalt takes fire in **chlorine**, and burns without incandescence; H. Rose added that finely-divided cobalt ignited in chlorine gas, forming blue, scaly crystals. W. Guertler and T. Liepus found that cobalt is attacked during 18 hrs'. exposure to chlorine water. J. B. Berthemot observed that when cobalt is heated to dull redness in the vapour of **bromine**, cobaltous bromide is formed. J. Nicklès said that the metal is scarcely attacked by a soln. of bromine in ether. O. L. Erdmann obtained the iodide by heating a mixture of finely-divided cobalt and **iodine**; and C. Winkler observed that cobalt iodide is formed by the action of a soln. of iodine and potassium iodide on cobalt. R. G. van Name and co-workers studied the rate of dissolution of cobalt in an aq. soln. of iodine and potassium iodide. G. Tammann discussed the formation of surface films by iodine vapour. H. E. Fierz-David found that, unlike iron, cobalt in association with iodine is not a satisfactory catalyst for the chlorination of benzene derivatives. A. D. White found that a soln. of **calcium hypochlorite**, of sp. gr. 1.04, gives off almost pure oxygen in contact with cobalt; and **hypochlorous acid** under similar conditions yields oxygen, chlorine and cobalt hydroxide and chloride. F. A. C. Gren observed that hot or cold **hydrofluoric acid** does not dissolve cobalt. Cobalt readily dissolves in **hydrochloric acid** with the evolution of hydrogen. J. Thomsen said the vigour of the reaction is between that of cadmium and tin. The order of the reaction with increasing vigour being Sn-Ni-Co-Cd-Fe-Zn. The action of the acid is augmented if the cobalt be platinized, or in contact with platinum. J. M. Weeren made similar observations with respect to the action of acids on cobalt, as were made in the case of zinc. W. A. Lampadius found that cold, fuming hydrochloric acid acts slowly on cobalt, forming a blue soln., and giving off hydrogen; the action is quicker with the hot acid, and an indigo-blue soln. is formed. W. Rohn observed that 99.5 per cent. cobalt, in contact with cold, 10 per cent. hydrochloric acid, lost 0.08 grm. per sq. dm. in 24 hrs., and 2.3 grms. per sq. dm. in 1 hour in the hot acid. W. Guertler and T. Liepus also found that cobalt is attacked during 8 hrs'. exposure to 10 or 36 per cent. hydrochloric acid. H. E. Patten found that cobalt is corroded by a soln. of hydrogen chloride in ethyl chloride, but not by a soln. in silicon tetrachloride, phosphorus trichloride, or antimony pentachloride. L. V. Pisarjehewsky, and M. A. Rozenberg and V. A. Yuza observed that a magnetic field retards the dissolution of cobalt in hydrochloric acid.

C. Frick,<sup>5</sup> E. Schürmann, E. V. Britzke and A. F. Kapustinsky, and W. Guertler studied the affinity of **sulphur** for cobalt. J. L. Proust, and T. Hiortdahl observed that sulphur unites with red-hot cobalt to form a fusible sulphide. The effect of sulphur on the properties of the metal was studied by B. Bogitch. J. Jahn observed that when cobalt is exposed to **hydrogen sulphide** at :

	100°	151°	198°	248°	311°	413°
Cobalt . . . . .	2963.4	2974.8	2974.0	2975.1	2975.8	2977.3 mgrms.
Gain in weight . . . . .	0.1	0.1	0.2	0.7	1.5	15.3 „

G. Tammann and W. Köster observed no change in the appearance of the metal after exposure to hydrogen sulphide and air at ordinary temp. H. Gruber observed



that the increase in weight of cobalt plates,  $60 \times 13 \times 12$  mm., after 1 hour's exposure to hydrogen sulphide :

	700°	800°	900°	1000°
Increase in weight . . .	3.7	7.6	4.9	destroyed

H. E. Patten observed that cobalt is not acted on by **sulphur monochloride**, and E. H. Harvey observed no attack during 52 weeks' exposure; and N. Domanicki said that the attack is very slow, if any. P. Nicolardot did not detect any action below  $136^\circ$ ; and with a soln. of the monochloride in ether, the attack, if it occurs at all, is very slow. W. Guertler observed that cobalt is attacked during 8 hrs'. exposure to a 10 or a 50 per cent. soln. of **sodium sulphide**, or to a 4 per cent. soln. of sodium sulphide mixed with 8 per cent. of sodium hydroxide. E. Priwoznik observed that cobalt is very little attacked by a soln. of **ammonium sulphide**. E. Beutel and A. Kutzelnigg studied the surface films produced by heating the metal in contact with the **sulphides of copper, silver, mercury, and lead**. According to J. Uhl, when heated in a current of **sulphur dioxide**, cobalt is partially transformed into sulphide. J. Jahn observed that when cobalt is exposed to moist air and dry sulphur dioxide at :

	100°	149°	199°	250°	297°	417°	circa
Moist { Cobalt . . .	748.2	748.2	739.2	1411.3	1411.5	3945.0	mgrms.
Moist { Gain in weight . . .	0	0.2	0.3	0.3	0.3	2.2	"
Dry { Cobalt . . .	2963.1	—	1411.8	—	3943.4	1412.1	"
Dry { Gain in weight . . .	0.1	—	0.3	—	0.5	0.7	"

Observations were also made by J. Uhl. When cobalt is heated with **sulphurous acid** in a sealed tube, at  $200^\circ$ , cobalt sulphide and sulphur are formed; the reaction was studied by C. Geitner. C. Dufraisse and D. Nakae studied the catalytic oxidation of soln. of sodium sulphite. Cobalt is readily dissolved by **sulphuric acid** with the evolution of hydrogen—*vide supra*, hydrochloric acid. W. A. Lampadius observed that sulphuric acid of sp. gr. 1.700 does not attack the metal in the cold, and the action is slow with the hot acid. The acid is first coloured amethyst-blue, and when the liquid is evaporated, heptahydrated cobaltous sulphate is formed. W. Rohn observed that with cold, 10 per cent. sulphuric acid, and 99.5 per cent. cobalt, 0.06 grm. per sq. dm. is dissolved in 24 hrs., and with the hot acid, 0.30 grm. is dissolved in 1 hour. W. Guertler and T. Liepus observed that cobalt is attacked during 8 hrs'. exposure to 10 per cent. sulphuric acid, or to 20 per cent. sulphuric acid sat. with sodium sulphate. R. H. Adie observed that with hot sulphuric acid, sulphur dioxide, but no hydrogen sulphide, appears at  $240^\circ$ . W. R. E. Hodgkinson and N. E. B. Bellairs found that when cobalt is heated with **ammonium sulphate**, some sulphite is formed; and W. Smith, that ammonium hydrosulphate is produced. E. Beutel and A. Kutzelnigg studied the films produced by a boiling soln. of **sodium thiosulphate** and lead acetate. M. G. Levi and co-workers, and O. Aschan and G. V. Petrelius found that cobalt is dissolved by soln. of **potassium** or **ammonium persulphate** without the evolution of gas, and rather more slowly than is the case with nickel. J. J. Berezeliu, and G. Little found that a heated mixture of cobalt and **selenium** combines with incandescence at a red-heat; and **tellurium** acts in an analogous manner. V. Lenher and C. H. Kao found that cobalt is not attacked by **selenium monochloride** at  $100^\circ$ ; W. L. Ray said that **selenium oxydichloride** acts very slowly; and V. Lenher, that **selenium oxydibromide** does not act on cobalt in a sealed tube at  $100^\circ$ .

A. Sieverts and co-workers<sup>6</sup> observed that **nitrogen** does not react with cobalt at temp. up to  $1150^\circ$ , and that the vol. of nitrogen occluded at :

	15°	200°	500°	700°	800°	900°	1000°
Hydrogen . . .	1.09	1.27	1.21	1.41	1.49	1.58	1.76 c.c.

L. R. Ingersoll observed that a nitride is formed when cobalt is spluttered in nitrogen; and H. N. Warren, and G. Tammann measured the rate of formation

of the nitride. L. R. Ingersoll and J. D. Hanawalt measured the X-radiogram before and after the adsorption—*vide supra*. O. Meyer observed that cobalt is but slightly attacked by **titanium nitride** at 1600°. F. Vorster found that cobalt decomposes **ammonia** into nitrogen and hydrogen when it is heated in that gas. G. T. Beilby and G. G. Henderson also found that cobalt decomposes ammonia at 470°. P. Sabatier found that cobalt forms a nitride when heated in ammonia to 470°, and the nitride is decomposed at 600°. W. Traube and B. Löwe, and C. Matignon and G. Desplantes observed that reduced cobalt in air for 40 hrs. is oxidized in the presence of aq. ammonia, and a brown soln. is formed. W. R. E. Hodgkinson and N. E. B. Bellairs found that in the presence of air, cobalt dissolves in aq. ammonia with the gradual formation of a nitride. W. Guertler and T. Liepus observed that 10, 50, and 70 per cent. aq. ammonia attacked cobalt in 8 hrs. The use of cobalt oxide as a catalyst in the oxidation of ammonia was studied by U. B. Bray. F. W. Bergstrom observed that cobalt shows no sign of attack when immersed in a soln. of **potassium amide** in liquid ammonia. W. R. E. Hodgkinson found that cobalt wire or foil is oxidized by molten **hydrazine hydrate**, reduced cobalt gives no explosion, but cobalt cubes produce an explosion. J. C. Roldan found that **hydroxylamine** in non-alkaline soln. acts on cobalt, producing an orange-red precipitate. P. Sabatier and J. B. Senderens found that reduced cobalt decomposes **nitrous oxide** incompletely at 230°, forming cobaltous or cobaltous oxide; it reacts at 150°, with **nitric oxide**; and at ordinary temp., **nitrogen peroxide** forms  $\text{Co}_3\text{O}_4$ , and at 500°,  $\text{Co}_4\text{O}_6$ —*nitro-cobalt*,  $\text{Co}_2(\text{NO}_2)_2$ , analogous to nitro-copper was obtained by P. Sabatier and J. B. Senderens, but the work of J. R. Park and J. R. Partington makes it doubtful if the nitro-cobalt is a chemical individual. F. Emich found that cobalt burns when heated in nitric oxide. P. Sabatier observed that **nitrosyl disulphonic acid**,  $\text{NO}(\text{HSO}_3)_2$ , converts cobalt into a cobaltic salt.

W. A. Lampadius observed that **nitric acid** of sp. gr. 1.30 attacks the metal in the cold, forming a dark red soln. of cobalt nitrate; and W. Hittorf noted that the action with an acid of sp. gr. 1.20 and less, is feeble. E. St. Edme found that cobalt becomes passive to nitric acid when it has been heated to redness in nitrogen gas. According to J. J. Acworth and H. E. Armstrong, conc. nitric acid attacks cobalt readily, but the 1:2-acid attacks the metal very slowly. W. Rohn found that cold, 10 per cent. nitric acid dissolves 10.7 grms. per sq. dm. in 24 hrs., whilst the hot acid dissolves 27.3 grms. per sq. dm. in 1 hr.—*vide supra*, the passive state. J. J. Acworth and H. E. Armstrong found that when the 1:2-acid attacks cobalt, the gas which is evolved—18.58 c.c. per gram at 18°—contains 5.71 per cent. NO; 79.23 per cent.  $\text{N}_2\text{O}$ ; and 15.06 per cent.  $\text{N}_2$ . C. Montemartini found that a gram of cobalt in 27.5 per cent. nitric acid, yields 0.02538 gm.  $\text{NH}_3$ ; 0.00077 gm.  $\text{HNO}_2$ ; 0.00929 gm.  $\text{N}_2\text{O}$ ; and 0.00467 gm.  $\text{N}_2$ . With 42.8 per cent. nitric acid, 0.01839 gm. ammonia was produced per gram of metal. It is said that the data do not agree with the assumption that the dissolution of the metal is accompanied by the formation of nascent hydrogen, or with the assumption that the metal is directly oxidized by the acid, rather does the nitric acid, in conjunction with the water present, act as an oxidizing agent. No hydroxylamine was observed in the final products of the reaction, so that if this compound is formed, it is again destroyed by secondary actions. The nitric oxide is of secondary origin, being formed by the decomposition of the nitrous acid. E. Ramann said that some cobaltous nitrate first formed by the action of nitric acid on cobalt, reacts:  $4\text{Co}(\text{NO}_3)_2 + 8\text{H}_2\text{O} + 11\text{Co} = 4\text{NH}_4\text{NO}_3 + 5\text{Co}_3\text{O}_4$ . W. Guertler and T. Liepus observed that cobalt is attacked during 8 hrs. exposure to 10 and 50 per cent. nitric acid, and also to aqua regia. C. C. Palit and N. R. Dhar studied the rate of dissolution of cobalt in nitric acid; and A. Quartaroli observed that the presence of urea slows down the action of nitric acid; but H. J. Prins found an acceleration in the attack of cobalt by acids in the presence of benzaldehyde or nitrobenzene. F. A. C. Gren observed that **aqua**

**regia** dissolves cobalt in the cold, forming a soln. the colour of peach blossom. W. R. E. Hodgkinson and N. E. B. Bellairs found that when heated with molten **ammonium nitrate**, cobalt furnishes a little hydrogen and ammonia; and W. Smith observed that the molten nitrate attacks the metal. F. W. Bergstrom, and H. Ehrig studied the solubility in an ammoniacal solution of ammonium nitrate.

B. Pelletier<sup>7</sup> found that **phosphorus** unites with red-hot cobalt to form a phosphide. S. F. Schemtschuschny and I. Schepeleff noted that a mixture of powdered cobalt and red phosphorus becomes warm at ordinary temp., presumably owing to the beginning of a reaction. A. Sieverts and M. Major found that cobalt reduced from the oxide, catalytically oxidizes soln. of **hypophosphites** with the evolution of hydrogen and the formation of some phosphoric acid. W. Rohn observed that 10 per cent. **phosphoric acid** dissolves 0.06 grm. of cobalt per sq. dm. in the cold in 24 hrs., and 0.7 grm. per sq. dm. in 1 hr. when heated. F. A. C. Gren said that cobalt is not attacked by a hot or cold soln. of phosphoric acid. A. Granger observed that the vapour of **phosphorus trifluoride** converts cobalt into phosphide; and likewise also **phosphorus tribromide**. A. F. Gehlen, C. J. B. Karsten, and T. Bergman observed that when **arsenic** is heated with cobalt, an arsenide is formed. A. F. Gehlen obtained an analogous result with **antimony** and cobalt; and K. Lewkonja, with **bismuth** and antimony. According to L. Kahlenberg and J. V. Steinle, at ordinary temp. **arsenic trichloride** slowly deposits a little arsenic on cobalt, and at 100° there is a slight reaction. F. A. C. Gren observed that **arsenic acid** dissolves a little cobalt.

M. Feszczenko-Czopowse<sup>8</sup> studied the cementation of cobalt by **boron**. H. Moissan observed that boron unites with cobalt at a high temp., forming a boride; and F. A. C. Gren found that a **boric acid** soln., cold or hot, does not attack cobalt. C. Winkler, and H. Moissan found that at a high temp. a compound of **silicon** and cobalt is formed; B. Boren studied the lattice structure of the cobalt silicides; R. Vogel and K. Rosenthal, the equilibrium diagram—*vide* the silicides.

H. E. Patten observed that **silicon tetrachloride** has no action on cobalt. W. Wahl observed that purified, finely-divided cobalt attacks **porcelain** when first melted; commercial cobalt, possibly because of the presence of some oxide, when melted in a porcelain crucible, forms a deep blue, glassy slag. P. Schützenberger and A. Colson,<sup>9</sup> G. Boecker, and O. Ruff and co-workers found that cobalt unites with **carbon**, and the reaction has been discussed in connection with carbides—5. 39, 20. F. Fischer and H. Bahr studied the carbide; and G. Tammann and K. Schönert, the diffusion of carbon in the metal. G. Boecker said that the saturation point for soln. of carbon in cobalt is 3.9 per cent. with a eutectic at 1300° and 2.9 per cent. of carbon. W. Nowacki studied the lattice structure of **cobalt tritacarbide**,  $\text{Co}_3\text{C}$ . O. Meyer observed that cobalt is attacked by **carbides**—silicon, molybdenum, and chromium at 1600°. I. L. Bell found that cobalt reacts less readily than nickel when it is heated with **carbon monoxide**, and a little carbon is formed:  $2\text{CO} = \text{C} + \text{CO}_2$ . P. Sabatier and J. B. Senderens said that the reaction occurs at 310°, and is almost complete at 420°, without the formation of a sublimate. The reaction was studied by R. Schenck and co-workers, and S. Kodama, and V. Kohlschütter and A. Nägeli observed that carbon is deposited at about 500°. E. F. Armstrong and T. P. Hilditch studied the reaction:  $\text{CO} + 3\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O}$ , when activated by cobalt; C. M. Loane, the catalytic oxidation of carbon monoxide; and A. Erdely and A. W. Nash, the hydrogenation of water-gas. L. Mond and co-workers observed that, unlike nickel, cobalt does not form a carbonyl at atm. press., but at higher press., volatile cobalt tetracarbonyl is formed. H. S. Taylor and R. M. Burns found that 1 vol. of cobalt at 25°, 110°, and 218° absorbs respectively 1.05, 0.60, and 0.35 vol. of carbon monoxide. F. Fischer and H. Bahr, K. Fujimura, and H. A. Bahr and V. Jensen studied the reduction of the oxide by carbon monoxide and the fission of that gas by cobalt. Cobalt does not dissociate carbon monoxide at 225°. E. C. White and J. F. Schultz, J. C. W. Frazer, and H. Remy studied the action of cobalt as a catalyst in oxidizing carbon

monoxide, etc. I. L. Bell found that at a red-heat, **carbon dioxide** is reduced to the monoxide by cobalt. W. Guertler and T. Liepus observed that carbon dioxide and air attack cobalt in 8 hrs. R. Schenck and H. Wesseldonk found that cobalt has no appreciable action on carbon dioxide at 600°, and at 900° about 5 per cent. of carbon monoxide is formed. P. H. Emmett and J. F. Schultz studied the equilibrium in the reaction:  $\text{Co} + \text{CO}_2 \rightleftharpoons \text{CoO} + \text{CO}$  at different temp. The constants,  $K = [\text{CO}_2]/[\text{CO}]$ , for the reactions at 450° and 570° are, respectively, 489.6 and 148.4. T. Bergman observed that an aq. soln. of carbon attacks cobalt slowly. Magnesia or manganese oxide accelerates the action, so that 40 per cent. of carbon monoxide is formed at 600°. Lime has no effect. N. I. Nitikin studied the adsorption of carbon dioxide by cobalt. E. P. Carpenter, J. R. Campbell and T. Gray, and W. P. Yant and C. O. Hawk studied the catalytic oxidation of **methane** by cobalt. F. Eisenstecken, and R. Schenck and co-workers studied the action of cobalt on methane. H. S. Taylor and R. M. Burns found that 1 vol. of cobalt at 25°, 110°, and 218°, absorbs respectively <0.50, 0.05, and <0.05 vol. of carbon dioxide; and respectively 0.35, 1.10, and <0.05 vol. of **ethylene**. R. N. Pease and L. Stewart, R. N. Pease and H. S. Taylor, and H. Hollings and R. H. Griffith studied the adsorption of hydrocarbons; and H. W. Walker, the reduction and polymerization of ethylene by cobalt at 400° to 450°; and O. Schmidt, the hydrogenation of hydrocarbons with cobalt as catalyst. H. Moissan and C. Moureu found that pyrophoric cobalt decomposes **acetylene** in the cold, and the metal becomes incandescent; some acetylene polymerizes to benzene, and some forms carbon and hydrogen. M. E. Kinsey and H. Adkins studied the catalytic decomposition of **acetaldehyde** by cobalt; F. Fischer and H. Koch, the catalytic synthesis of **benzene**; and J. H. Long, the hydrogenization of benzene. E. W. Kanning and O. W. Brown, the catalytic decomposition of **kerosene** by cobalt. H. E. Patten found that cobalt was tarnished by **ethyl chloride**. G. F. Hüttig and R. Kassler found that in the decomposition of **formic acid** with cobalt prepared in different ways as catalyst, the catalytic activity is conditioned by the temp. of reduction of the oxide. The difference is negligible with temp. between 300° and 550°; but if the reduction temp. is 1000° to 1200°, the activity of the metal is considerably diminished. The metal produced by reducing the hydroxide was rather more active than when obtained by calcining the nitrate. W. Rohn observed that 10 per cent. **acetic acid** dissolves 0.04 grm. per sq. dm. in 24 hrs. in the cold, and 0.15 grm. per sq. dm. in 1 hr. when heated. F. A. C. Gren observed that cobalt is not dissolved by cold or hot acetic acid, but C. Schall and H. Markgraf found that 4 hrs'. action at ordinary temp. dissolves about 0.0021 grm. of cobalt (per 6.5 sq. cm.). F. A. C. Gren observed that **oxalic acid** dissolves cobalt in the cold. W. Guertler and T. Liepus found cobalt is attacked after 8 hrs'. exposure to acetic acid, **citric acid**, and **tartaric acid**. G. Dupont and J. Allard studied the autoxidation of **abiatic acid** in the presence of cobalt. C. B. Gates said that cobalt is not attacked by **oleic acid** between 90° and 100°. A. Brochet and J. Petit studied the dissolution of a cobalt anode in a soln. of **potassium cyanide** under the influence of an alternating current. C. Kelber observed that finely-divided cobalt can be used like nickel (*q.v.*) as a catalyst in the hydrogenation of many compounds, but the reaction proceeds rather more slowly. C. Dufraisse and D. Nakae studied the catalytic oxidation of acetaldehyde, phenylaldehyde, furfuraldehyde, styrene, and turpentine. A. Benedicenti and co-workers, and G. B. Bonino and co-workers found that powdered cobalt unites with the **proteins** when shaken with a soln. of egg-albumin or blood-serum. L. L. Steele studied the effect of cobalt soap on the drying of **linseed oil**; and W. Thomson and F. Lewis observed no effect on **india-rubber**. A. Simon and K. Kötschau observed that finely-divided cobalt with benzidine and **guaiacum resin** gives a blue coloration, indicating the formation of hydrogen dioxide.

K. A. Hofmann and H. Hiendlmaier<sup>10</sup> found that cobalt is readily attacked by burning **potassium**. W. G. Imhoff studied the corrosive action of molten **zinc**

on cobalt. According to C. Tubandt, cobalt is not attacked by **potassium or sodium hydroxide**, hot or cold, but if the metal be the anode to an electric current, it dissolves in the alkaline liquid. The most favourable conditions for the dissolution are a low current density—0.2 amp. per sq. dm.—a high temp., and a highly conc. soln. The cobalt dissolves as a cobaltous salt. For the anodic dissolution of cobalt in 8*N*-KOH, resulting, according to G. Grube and O. Feucht, in the formation of a dark blue soln. of potassium cobaltite, *vide supra*, the anodic behaviour of cobalt. M. le Blanc and O. Weyl observed that when cobalt is fused with potassium hydroxide in an atm. of nitrogen at 550° to 560°, there is a perceptible reaction although no water, hydrogen, or potassium has been detected in the product. C. Winkler observed that if the cobalt has been prepared by reduction at a low temp. from the precipitated oxide, hot potash-lye forms a dark blue soln. W. Guertler and T. Liepus observed that in 8 hrs. cobalt is attacked by 10 and 50 per cent. soln. of sodium hydroxide, and by a mixture of soda-lye and hydrogen dioxide. H. Moissan found that in the electric arc-furnace cobalt is oxidized by molten **calcium oxide**. C. B. Gates observed that cobalt does not react with molten **calcium chloride**. W. Guertler and T. Liepus found that cobalt is attacked during 8 hrs'. exposure to a soln. of **magnesium chloride**. E. Ramann observed that powdered cobalt acts on **cobaltous nitrate**, giving a dark-coloured precipitate; and when warmed, ammonia is evolved and the precipitate becomes pale red. J. B. Senderens observed that when a soln. of **copper, silver or lead nitrate** is treated with cobalt, the amount of cobalt passing into soln. is greater than corresponds with the equation:  $M(NO_3)_2 + Co = Co(NO_3)_2 + M$ . The excess is slight with silver, and is negligible if air be excluded. In the other cases, the metal oxidizes at the expense of the nitric acid present, forming a hydroxide or basic nitrate. W. Eidmann observed that a soln. of **cupric chloride** in acetone acts slowly on cobalt, forming cuprous and cobaltous chlorides. C. B. Gates found that copper is precipitated from fused **copper palmitate** by cobalt; a little copper is precipitated from **copper stearate**; and none from **copper margarate**. C. B. Gates observed that cobalt reacts with molten **silver nitrate or chloride** with the separation of silver. C. Winkler, and G. Krüss and F. W. Schmidt found that cobalt acts on a neutral soln. of **gold chloride**, precipitating yellowish-brown gold free from cobalt, but if alkalies are present, cobaltiferous gold is precipitated. W. Guertler and T. Liepus found that a 1:500-soln. of **mercuric chloride** is decomposed by cobalt. E. Alexander observed that a soln. of mercuric chloride in ethyl acetate does not attack cobalt. J. Napier found that cobalt reduces soln. of **ferric chloride** to the metal. T. Heymann and K. Jellinek studied the equilibrium conditions in the reaction:  $Co + Ni^{++} \rightleftharpoons Ni + Co^{++}$  with soln. of **nickel nitrate and sulphate**. M. Curie and J. Saddy studied the inhibition of the luminescence of the **zinc sulphide** phosphor by the presence of cobalt.

**Some reactions of analytical interest.**—Soln. of cobaltous salts give no precipitate with **hydrogen sulphide** if free acids are present; and if the soln. is neutral, a part of the cobalt is slowly precipitated as a hydrated cobaltous sulphide. A soln. of cobaltous acetate in the presence of acetic acid gives either no precipitate or only a very small one, but in the absence of free acid, the precipitation is complete or almost complete. If the soln. contains an excess of alkali acetate, and free acetic acid is absent, all the cobalt may be precipitated by hydrogen sulphide from hot soln. Free tartaric, citric, monochloroacetic, or formic acid also hinder the precipitation, but the alkali salts of these acids enable the precipitation to be made from hot soln. This subject was discussed by H. Baubigny,<sup>11</sup> H. Delffs, A. Terreil, A. Villiers, L. L. de Koninck, F. Field, and O. F. Tower. Hydrogen sulphide in alkaline soln., or a soln. of **alkali or ammonium sulphide or hydrosulphide** gives a black precipitate of hydrated cobaltous sulphide. The precipitation is favoured by ammonium sulphide. The precipitate is insoluble in alkali and ammonium sulphides, it is very slightly soluble in acetic acid, and it dissolves with difficulty in hydrochloric acid, and particularly so if the precipitation has been

made from hot soln. Hot nitric acid and aqua regia dissolve the precipitate. This subject was discussed by A. Terreil, H. W. F. Wackenroder, F. Field, and G. Chesneau. According to F. Jackson, the reaction with ammonium sulphide is sensitive to 1 : 512,000, and, according to C. H. Pfaff, 1 : 200,000. C. D. Braun found that **potassium thiocarbonate** colours ammoniacal, conc. soln. of cobaltous salts brown or black, and dil. soln. yellow. P. Berthier found **potassium sulphite**, but not **ammonium sulphite**, gives an incomplete precipitation of a basic sulphite. P. Falciola, and W. Heinz observed red colorations with ammoniacal soln. of cobalt salts and **sodium hydrosulphite**. O. Brunck observed that **sodium hyposulphite** precipitates cobalt sulphide from neutral, ammoniacal, or acetic acid soln., but not in the presence of mineral acids. H. Marshall found **persulphates** precipitate cobaltic oxide. Acidic soln. give no precipitate with **sodium thiosulphate**, and with neutral soln., an incomplete precipitation of cobaltous sulphide occurs after a prolonged boiling. The reaction was studied by O. W. Gibbs, F. Faktor, W. Ball, and A. Terreil.

Cobaltous salt soln. give a blue precipitate of a basic salt:  $\text{CoCl}_2 + \text{KOH} = \text{KCl} + \text{CoCl}(\text{OH})$ , when treated in the cold with **potassium or sodium hydroxide**, but on warming, pink cobaltous hydroxide is precipitated. With moderately conc. soln., the pink precipitate may be produced in the cold, or after the soln. has stood some time. The rate of precipitation is dependent on the conc. of the alkali-lye. F. Jackson said that the reaction with sodium hydroxide is sensitive to 1 : 16,000. Cobaltous hydroxide, unlike the corresponding nickel hydroxide, gradually turns brown on exposure to air, owing to oxidation:  $2\text{Co}(\text{OH})_2 + \text{H}_2\text{O} + \text{O} = 2\text{Co}(\text{OH})_3$ . If alcohol and alkali-lye be added to the soln. of a cobaltous salt, and the mixture is boiled, dark brown cobaltic hydroxide is quickly formed. The presence of ammonium chloride hinders the precipitation by alkali hydroxide. The precipitated hydroxide or basic salt dissolves completely in a soln. of ammonium carbonate to form a violet-red soln. This subject was studied by A. Remelé, F. Reichel, E. Donath, H. Ditz, C. Winkler, and G. C. Winkelblech. Cobaltous hydroxide is peptized or dissolved by a very conc. soln. of alkali hydroxide, forming a blue liquid. This was examined by E. Donath, and C. Tubandt. H. Demarçay observed that **magnesium oxide** gives a precipitate with warm cobalt salt soln. In the absence of ammonium salts, aq. **ammonia** precipitates a blue basic salt from soln. of cobaltous salts, and the precipitate is soluble in soln. of ammonium chloride. Citric and tartaric acids hinder the precipitation. The dirty yellow, ammoniacal soln. gradually turns a reddish colour on exposure to air. The reaction was studied by F. Field, and H. Ditz. A reddish basic salt, of varying composition, is precipitated from cobaltous salt soln. by **alkali carbonates**; and the reddish, basic salt precipitated by **ammonium carbonate** is soluble in excess. The subject was studied by F. Field. According to J. N. von Fuchs, and G. C. Winkelblech, cobalt salts are not precipitated when they are heated with calcium carbonate, or boiled with strontium carbonate; H. Demarçay found that the **alkaline earth carbonates** and magnesium carbonate do not precipitate cobalt salts in the cold, but they do so above 75°. J. W. Döbereiner also noted the precipitation with **magnesium carbonate**. Barium carbonate and bromine give a black precipitate of cobaltic oxide, with cobaltous salts, but not so with nickel salts.

When **oxidizing agents**—chlorine, bromine, hypochlorites, hypobromites, hypiodites, barium dioxide, hydrogen dioxide, etc.—are added to an alkaline soln. of a cobalt salt, cobaltic hydroxide is immediately precipitated:  $\text{Co}(\text{OH})_2 + \text{NaOH} + \text{Cl} = \text{NaCl} + \text{Co}(\text{OH})_3$ . These reactions were studied by O. Popp, A. Terreil, F. Field, C. D. Braun, E. and B. Klimenko, E. P. Alvarez, W. Kwasnick, C. Reichard, R. G. Durrant, C. C. Palit, A. Job, A. Jaworowsky, T. Poleck, G. Kassner, O. W. Gibbs, F. Gauhe, H. Rose, and R. L. L. Taylor. The precipitation with **potassium iodate** was studied by S. R. Benedict, and S. E. Moody.

When conc. soln. of cobalt salts, acidified with acetic acid, are treated with **potassium nitrite**, a yellow crystalline precipitate is formed; with dil. soln., the

precipitation occurs only after the mixture has stood for some time. The reaction is supposed to take place in stages—first the formation of nitrous acid:  $\text{CoCl}_2 + 2\text{KNO}_2 \rightleftharpoons \text{Co}(\text{NO}_2)_2 + 2\text{KCl}$ , and  $2\text{KNO}_2 + 2\text{CH}_3\text{COOH} = 2\text{CH}_3\text{COOK} + 2\text{HNO}_2$ ; the oxidation of cobaltous nitrite to cobaltic nitrite:  $\text{Co}(\text{NO}_2)_2 + 2\text{HNO}_2 = \text{H}_2\text{O} + \text{NO} + \text{Co}(\text{NO}_2)_3$ ; and finally, the formation of the complex salt:  $\text{Co}(\text{NO}_2)_3 + 3\text{KNO}_2 = \text{K}_3\text{Co}(\text{NO}_2)_6$ . This reaction is used for the detection of cobalt salts in the presence of nickel salts, and it was studied by N. W. Fischer, S. Evre, O. L. Erdmann, A. Duflos and N. W. Fischer, S. Tanatar and S. Petroff, H. Yagoda and H. M. Partridge, C. D. Braun, etc.—*vide supra*, the separation of cobalt and nickel.

Neutral soln. of cobalt salts give with **potassium cyanide** a reddish-brown precipitate which is soluble in excess in the cold, forming a brown soln. of potassium cobaltocyanide,  $\text{CoCl}_2 + 2\text{KCy} = 2\text{KCl} + \text{CoCy}_2$ , and  $\text{CoCy}_2 + 4\text{KCy} = \text{K}_4\text{CoCy}_6$ . When the brown soln. is warmed for some time, it becomes yellow, and alkaline, owing to the formation of cobalticyanide:  $2\text{K}_4\text{CoCy}_6 + \text{H}_2\text{O} + \text{O} = 2\text{KOH} + 2\text{K}_3\text{CoCy}_6$ . The oxidation proceeds more quickly in the presence of oxidizing agents—*e.g.*, chlorine, hypochlorites, etc. An excess of the oxidizing agent decomposes the nickel but not the cobaltic salt. The cobaltocyanide is decomposed by hydrochloric acid, but not so the cobalticyanide. The cobalticyanide forms sparingly soluble salts with most of the heavy metals—*e.g.*, cobaltous (pink) and nickel (green) cobalticyanides are formed. If a mixed soln. of cobalt and nickel salts be treated with an excess of potassium cyanide, and the boiling soln. be treated with hydrochloric acid, green nickel cobalticyanide is precipitated:  $2\text{K}_3\text{CoCy}_6 + 3\text{K}_2\text{NiCy}_4 + 12\text{HCl} = 12\text{KCl} + 12\text{HCy} + \text{Ni}_3(\text{CoCy}_6)_2$ . The reaction was studied by J. von Liebig, F. Wöhler, J. Tattersall, G. Papasogli, C. Krauss, E. P. Alvarez, O. W. Gibbs, F. Gauhe, etc.—*vide supra*, the separation of cobalt and nickel. A. Remelé showed that **potassium ferrocyanide** gives a dark greyish-green precipitate with cobaltous salts, and when the mixture is boiled in air, it becomes dark blue; the brownish-red precipitate with **potassium ferricyanide** under similar conditions becomes dark green. The reaction was studied by W. Skey, R. H. Davies, A. H. Allen, L. Mindaljeff, F. F. Werner, and W. F. Gintl. R. Ripan, and B. J. F. Dorrington and A. M. Ward found that **potassium cyanate** gives a blue coloration. If a conc. soln. of **ammonium thiocyanate** be added to a soln. of a cobaltous salt, the colour changes to bright blue:  $\text{CoCl}_2 + 2\text{NH}_4\text{CyS} = 2\text{NH}_4\text{Cl} + \text{Co}(\text{CyS})_2$ , and  $\text{Co}(\text{CyS})_2 + 2\text{NH}_4\text{CyS} \rightleftharpoons (\text{NH}_4)_2\text{Co}(\text{CyS})_4$ . If water be added, the colour changes to pink; but if shaken with amyl alcohol and ether, the blue salt passes into the ethereal layer. The reaction was studied by H. W. Bettink, H. Ditz, F. W. Dootson, F. Feigl and R. Stern, M. Gorsky, R. Grassini, I. M. Kolthoff, T. T. Morell, A. D. Powell, A. Rosenheim and co-workers, N. Rusting, L. Schönn, G. Sensi and R. Testori, A. Simen, N. A. Tananaeff, F. P. Treadwell, H. W. Vogel, C. H. Wolff, and C. Zimmermann. The colour is sensitive to nearly 1 : 20,000. J. J. Fox precipitated cobalt quantitatively with **potassium selenocyanide**.

H. Weil observed that neutral soln. of cobalt salts with **potassium chromate** give a brownish-red precipitate of a basic chromate; A. Carnot obtained no precipitation with **ammonium molybdate**, or with **ammonium tungstate**. A. Liebersson obtained a blue coloration with **arsenatophosphotungstic acid** in the presence of a cyanide. P. Berthier obtained a blue precipitate with **sodium hydrophosphate**. C. D. Braun obtained a precipitate with **sodium pyrophosphate** in the presence of a hypochlorite. S. J. Jindal observed that **sodium silicate** gives a blue precipitate. Soln. of cobalt salts give a turbidity with **oxalic acid**, and C. H. Pfaff found that with **alkali oxalates**, the reaction is sensitive to 1 : 1000.

M. Ilinsky and G. von Knorre found that  **$\alpha$ -nitroso- $\beta$ -naphthol** gives a red precipitate with acetic acid soln. of cobalt salts. The reaction was studied by C. Krauss, C. Meineke, R. Fischer, F. W. Attack, L. L. de Koninck, H. Copaux, and W. H. Chapin—*vide supra*, the separation of nickel and cobalt. I. Bellucci said that  **$\beta$ -nitroso- $\alpha$ -naphthol** is more sensitive for cobalt than  **$\alpha$ -nitroso- $\beta$ -naphthol**.

O. Brunck observed that  **$\alpha$ -dimethylglyoxime** gives a precipitate with nickel but not cobalt salts in a strongly ammoniacal soln.—*vide supra*, the separation of nickel and cobalt—and it was studied by L. Tschugaeff, K. Kraut, F. Feigl and L. von Tustanowska, and G. Sensi and R. Testori. H. Grossmann and W. Heilborn found that **dicyanodiamidine sulphate** gives a precipitate of the nickel but not the cobalt salt in strongly ammoniacal soln.—*vide supra*, the separation of nickel and cobalt. G. Malatesta and E. di Nola found that cobalt, copper, and nickel salts give a blue coloration in ammoniacal soln. when treated with **1 : 2-diaminoanthraquinone-3-sulphonic acid**; W. R. Orndorff and M. L. Nichols, and M. L. Nichols and S. R. Cooper, a reddish- or bluish-violet coloration with **dinitrosoresorcinol**; C. Brenner obtained a blue coloration by **nitrosochromotropic acid**; H. S. van Klooster, a red coloration with sodium acetate and a soln. of a **nitroso-R-salt**; F. Kröhnke, a reddish-yellow coloration or precipitate with **isonitrosoacetophenone**; E. Eegriwe, an orange colour with **eriochrom blue black B**, and **eriochrom red B**; F. Feigl, a blue coloration or precipitate with **benzidine**; H. Fischer, a reddish- or bluish-violet colour with **diphenylthiocarbazone**; D. Vitali, a bluish-violet colour with potassium permanganate and **uric acid**; I. M. Kolthoff, a rose-red colour with **diphenylcarbazide**; W. Hieber and F. Leutert, a blue colour with **acetoxime**; R. Berg, a precipitate with o-oxyquinoline; and E. J. Fischer, a blue coloration with **glyoxaline**. K. W. Charitschkoff showed that a benzene soln. of **naphthenic acid** gives an eosin-red with cobalt salts. H. O. Jones and H. S. Tasker found that **potassium dithio-oxalate** gives a deep brown coloration with cobalt salts and a magenta-red with nickel salts sensitive to 1 : 8,000,000. J. L. Danziger obtained a blue colour with **ammonium thioacetate**—R. Schiff and N. Tarugi said that no precipitate is formed in acidic soln., but in ammoniacal soln., cobaltous sulphide is precipitated; and H. Hlasiwetz, T. L. Phipson, and A. del Campo and J. Ferrer, green precipitates with **potassium xanthogenate** or **potassium methylxanthogenate**. C. Vincent obtained blue precipitates with **dimethylaniline** and also with **trimethylamine**.

**The metallic precipitation of cobalt.**—A. C. Becquerel<sup>12</sup> observed that **copper**, immersed in a soln. of sodium cobalt chloride, acquires a film of cobalt. Z. Roussin observed that magnesium deposits cobalt with the evolution of hydrogen from slightly acidic soln. of cobalt salts. S. Kern noted that with cobalt chloride, a green basic salt is formed; and A. Commaille noted hydrated cobalt hydroxide is precipitated from soln. of the sulphate. According to D. Vitali, when a soln. of a cobalt salt is treated with magnesium, coloured flecks of the hydroxide are formed, and as the action continues, these are gradually reduced to the metallic state—*vide infra*, cobaltous chloride. According to N. W. Fischer, cobalt can be precipitated from soln. of its salts by **zinc** and **cadmium**, but not completely if hydrochloric acid be present, and not at all if nitric acid be present. A. C. Becquerel added that a boiling soln. of cobalt chloride or sulphate and an excess of zinc precipitates all the cobalt as a black powder; and J. L. Davies, and E. A. Demarçay found that the reaction is favoured if the soln. be ammoniacal. According to L. de Boisbaudran, although cobalt is not precipitated from its soln. by metallic zinc, the presence of a metal easily reduced by zinc determines the precipitation of the cobalt. Lead and copper both act in this way, the latter in particular; cadmium does not. The soln. should be very nearly neutral for copper to produce the maximum effect; if the liquid is very acid, the copper alone is deposited. In a soln. rendered very basic by lengthened contact with zinc, the cobalt is not only no longer precipitated, but actually re-dissolves, at the same time an insoluble salt of copper is produced. The addition of a very minute quantity of acid again decolorizes the soln. The cobalt is reduced to the metallic state; the metallic sponge is at first attacked by hydrochloric acid, but the action soon ceases, which indicates an intimate admixture of the copper and cobalt. The reaction was studied by G. Hänsel, A. Grevel, and N. Izgaruishef and I. Mirkin. A. A. Damour found that zinc amalgam deposits cobalt from neutral soln. of cobalt salts. F. Stolba



found that cobalt is deposited on steel or iron by contact with zinc in a boiling soln. of zinc chloride containing a cobalt salt; and C. Mène deposited cobalt on lead, iron, brass, and copper by immersing the metal in contact with zinc in a boiling soln. of zinc chloride containing fragments of cobalt. W. C. Reid observed that **thallium** deposits a basic salt from a soln. of cobalt nitrate.

**The physiological action of cobalt salts.**—In 1827, G. C. Gmelin<sup>13</sup> discussed the action of cobalt salts on the animal organism. According to E. Haselhoff, water containing 1 to 2 mgrms. of cobalt per litre exerts a toxic action on vegetation. The subject was discussed by M. Nakamura, and Y. Fukutome. According to J. Bock, the minimum dose of cobalt salts for frogs is 66 mgrms. per kgrm.; for rats, 20 mgrms.; and for guinea-pigs, 16 mgrms. T. Siegen found that 0.1 gm. of cobalt chloride or nitrate killed a frog in half an hour, and 0.3 gm. killed, in 3 hrs., a rabbit weighing 1.5 kgrms. J. Antal observed that only in conc. soln. are cobalt salts poisonous, and that they are quickly given off by the system. Thus, cobalt was detected in the urine 2 hrs. after administration. The subject was also examined by T. P. Anderson and T. P. A. Stuart, and F. Coppola, R. H. Chittenden and C. Norris observed that the poisonous action on rabbits is slow, and manifest only after the administration of relatively large doses. Death is caused by the stopping of the heart, and there also occur enteritis, and an interference with digestive processes. No action was observed on the liver or kidney. Paralysis of the extremities occurs. The cobalt salts form in great measure insoluble compounds with the proteids of the food, and are excreted with the faeces; part enters the circulation and is rapidly distributed to all parts of the body, and is eliminated ultimately in the urine. The body temperature is raised, and the peripheral cutaneous vessels are constricted. Among the organs, the spinal cord and brain stand first in their power of picking up and storing the metal. The muscular tissues also retain a larger percentage of the cobalt than the liver or kidneys. The muscular tissue of the back also retains a larger percentage than that of the legs. The lungs and heart also retain a high percentage of the metal. F. Wohlwill observed that cobalt causes a disturbance of the alimentary tract, and the accompanying nervous symptoms may be due to a direct action on the central nervous system. L. Massol and M. Breton found that the injection of a milligram of cobalt sulphate in the brain of a guinea-pig did not cause death. J. Antal observed that a gram of cobalt nitrate in 1 per cent. soln. had no perceptible effect on rabbits, but a gram in a 5 per cent. soln. killed a rabbit in 24 hrs. According to G. Bertrand and H. Nakamura, nickel and cobalt have a definite effect on animal metabolism; and P. Mascherpa found that when administered orally or subcutaneously, cobalt is absorbed by the organism, and excreted partly by the kidneys, and partly by the intestine. Y. Delage noted that cobalt chloride favours the parthenogenetic *Strongylocentrotus lividus*. C. Gerber studied the action of cobalt salts on the coagulation of milk by proteolytic enzymes. H. W. Armit studied the toxic action of cobalt carbonyl; A. Chassevant and C. Richet, the toxic action of cobalt salts on lactic fermentation; and E. Funk, the action on catalase and amylase ferments. The physiological action of cobalt was studied by G. Bertrand and co-workers, M. Labbé and co-workers, and F. Kraus and T. Brugsch. The physiological effect of some complex cobaltic ammino-salts was studied by J. Bock, and A. Oswald. Cobaltous nitrate has been used in subcutaneous injections, as an antidote to poisoning by cyanide.

**The uses of cobalt.**—Cobalt is not in extensive use.<sup>14</sup> Cobalt oxide is used for colouring enamels, glasses, and pottery, and other glazes blue. It is valuable for this purpose because the colour is stable in the presence of silicates, and at a high temp. Cobalt oxide, or, less frequently, smalt, is also used in preparing underglaze colours for producing the ultramarine type of blue—e.g., the so-called willow pattern; for tinting other colours; or for the so-called matt blue which approximates to the turquoise blue, and has cobalt aluminate as the basal stain. Cobalt oxide diluted with a large proportion of clay or flint and calcined, or a soluble cobalt

salt, is used as a stain to counteract or mask the cream colour produced by the traces of "iron" in the raw materials. Several preparations of cobalt have been used as pigments for painting. Their covering power is poor, and although they are usually very permanent, their comparatively high cost prevents them taking the place of other pigments.

A blue glass prepared in Saxony since the sixteenth century,<sup>15</sup> under the name *smalt*, *bleu d'azur*, or *bleu de saxe*, is essentially a potassium silicate glass coloured with cobalt. T. I. Bowler described the manufacture of smalt in China. In Saxony, the bismuth ferrous ore is heated to separate the bismuth by liquation; the crushed product is roasted to furnish a crude oxide called *zaffre* or *zaffler*. The zaffre is mixed with potassium carbonate and ground quartz or sand, and fused to a glass. The impurities settle at the bottom, and the blue glass is ladled off with iron spoons, and poured into cold water. The glass is then ground to powder, levigated, dried, and sifted. A cobalt aluminate blue, called *cobalt-blue*, *Thénard's blue*, *cobalt ultramarine* or *King's blue*, is prepared by calcining mixtures of cobalt oxide and alumina or ammonium-alum, or potash-alum. In the last case, the product is washed to remove the alkali sulphate. According to J. J. Berzelius,<sup>16</sup> the effect of alumina on the colour produced by cobalt was noticed by J. G. Gahn in 1777, and later by C. F. Wenzel. Zinc oxide, and phosphate may be added to the mixture before calcination. The original Thénard's blue was made with a cobalt phosphate or arsenate and alumina, but now the cobalt-aluminium blue has often the same designation.

The so-called *cerulean blue*, or *bleu céleste*, is produced by heating a mixture of cobalt sulphate, tin oxide, and precipitated silica or chalk. The green colour, called *Rinman's green*, *zinc green*, or *cobalt green*—*vide infra*, zinc percobaltite—is prepared by firing a mixture of cobalt and zinc oxides. The bluish-green pigment, called *turquoise green*,<sup>17</sup> is made by firing a mixture of cobalt oxide, chromic oxide, and alumina. The so-called *Indian yellow*, *aureolin*, or *cobalt yellow*, is potassium cobaltic nitrite—*vide* 8. 49, 38. The so-called *cobalt brown* is produced by calcining a mixture of ammonium, ferrous and cobalt sulphates. Cobalt arsenate or phosphate, when ground, furnishes a pink colour.<sup>18</sup> The calcination of precipitated magnesium carbonate stained with cobalt nitrate, furnishes the so-called *cobalt magnesite pink*; <sup>19</sup> and *cobalt bronze* is a violet ammonium cobalt phosphate with a bronze lustre.

A dil. soln. of the pink cobalt salts—chloride or nitrate—is used as a *sympathetic ink*,<sup>20</sup> *vide supra*—the writing on paper is invisible except when the paper is warmed. The anhydrous blue becomes invisible as the paper is cooled and atm. moisture is absorbed. Cobalt nitrate is used as a blowpipe reagent to assist in the recognition of compounds of aluminium, zinc, and magnesium. Some organic compounds of cobalt—*e.g.*, resinate, oleate, and acetate—have been used to facilitate the "drying" of oils, paints, and varnishes. A. and L. Lumière and A. Seyewitz<sup>21</sup> experimented on the toning of photographic plates with cobalt. The Nya Akkumulator Aktiebolaget experimented on the use of cobalt for the electrodes of accumulators; and R. Langhans, as a constituent in preparing thoria incandescent mantles. M. Baum deposited platinum on cobalt plating.

Owing to its pleasing colour, hardness, and resistance to tarnish, cobalt offers possibilities in electroplating, and in making coins. Cobalt is also employed in making alloys. The Fe<sub>2</sub>Co-alloy has valuable magnetic qualities, discussed by H. T. Kalmus and K. B. Blake.<sup>22</sup> Cobalt steels for magnets have been described by K. Honda and S. Saito. There are also special alloys with various trade names—*e.g.*, *iridium* is a cobalt-tungsten-chromium steel with less than 1 per cent. each of vanadium, molybdenum, and carbon; *stellite*, described by E. Haynes, was originally a chromium-cobalt (1 : 3) alloy. These alloys resist corrosion very well. Stellite was afterwards made with up to about 25 per cent. of tungsten, and also molybdenum. They are used for lathe tools. The so-called *cochrome* is a cobalt-chromium alloy used for electrical resistance wires. A cobalt-tin alloy is brittle but resists attack by acids. Cobalt is also added to strengthen brass, and

aluminium alloys. Cobalt amalgam is used in dentistry. The uses of cobalt alloys were described by J. Aston, W. R. Barklay, W. S. Barrows, L. Guillet, E. A. Watson, A. Haenig, etc.—*vide infra*.

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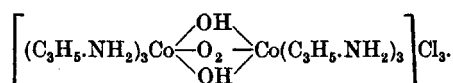
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### § 8. The Atomic Weight and Valency of Cobalt

W. Manchot and co-workers,<sup>1</sup> G. Grube, and L. Cambi and co-workers discussed the possibility of the existence of *univalent cobalt* in the nitrosyls; and the valency of cobalt was discussed by E. Thilo. Cobalt behaves as a *bivalent* element in the so-called cobaltous salts typified by cobaltous chloride,  $\text{CoCl}_2$ , which is unimolecular in pyridine soln., and bimolecular in urethane soln. This also is in agreement with the vapour density of cobaltous acetylacetonate,  $\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_2$ ; and with the isomorphism of the zinc, magnesium, manganese, and cobaltous sulphates of the type  $\text{MSO}_4 \cdot 6\text{H}_2\text{O}$ , discussed by W. Stortenbecker. Cobalt also behaves as a *tervalent* element in the so-called cobaltic salts. This is illustrated by the cobaltic acetylacetonate,  $\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_3$ , of G. Urbain and A. Debierne, who found that the salt is unimolecular in benzene soln. This is also confirmed by the existence of the cobaltic alums, and by the isomorphism of the potassium complex cyanides,  $\text{K}_3\text{CoCy}_6$ ,  $\text{K}_3\text{MnCy}_6$ , and  $\text{K}_3\text{FeCy}_6$ . Determinations of the mol. wts. of the cobaltic amines by the f.p. method, and observations on the electrical conductivities, etc., by S. M. Jørgensen, J. Petersen, A. Werner and A. Miolati, and W. Biltz agree with the assumption that the contained cobalt is tervalent. The double sulphates or alums of the type  $\text{R}_2\text{SO}_4 \cdot \text{Co}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ , studied by H. Copaux, J. L. Howe and E. A. O'Neal, and H. Marshall, isomorphous with the corresponding alums of tervalent iron, chromium, aluminium, and some of the platinum metals, all support the tervalency of cobalt. There are indications of a still higher valency in the so-called cobaltous acid,  $\text{H}_2\text{CoO}_3$ , and its salts observed by A. H. McConnell and E. S. Hanes, and E. Dufau; or the more doubtful cobaltic acid,  $\text{H}_2\text{CoO}_4$ .

According to N. V. Sidgwick, the highest co-valency of the atoms of the elements up to the end of the first long period of the periodic classification is 6. E. G. V. Percival and W. Wardlaw attributed a co-valency of 4 to some double salts of cobaltous chloride with quinoline, and pyridine. R. Weinland quoted A. Pieroni and A. Pinotti's complex salt as an example of a compound whose **co-ordination number** is 8 not 6, but W. R. Bucknall and W. Wardlaw showed that the original formulation of the salt was wrongly stated to be  $[\text{Co}(\text{C}_3\text{H}_5\text{.NH}_2)_3]\text{Cl}_3$ , it should be:



T. M. Lowry, and H. Reihlen discussed the subject. A. Werner prepared a series of optically active compounds of cobalt which show that their structure is asymmetric. P. Karrer, A. F. Richter, and A. Werner discussed the valency isomerism of cobalt.

Up to the year 1857, the generally accepted value for the at. wt. of cobalt was 58.9. The datum 58.9 due to J. J. Berzelius,<sup>2</sup> was based on the analysis of cobalt chloride; and it was found to be in agreement with the observations on the valency of cobalt, with the sp. ht., and with the isomorphism of various cobalt salts with salts of related elements. T. Thomson attempted to find the at. wt. of cobalt in 1821. The observed values for the at. wts. of iron (55.84), cobalt (58.97), and of nickel (58.68), do not fit in with the periodic law of D. I. Mendeléeff, for the at. wt. of cobalt should be less, not greater, than that of nickel, and greater than that of iron. This difficulty was attributed by H. Remmler, and G. Krüss and F. W. Schmidt to the presence of an unknown element, *gnomium*, but all attempts to establish the existence of the hypothetical element proved nugatory, and the hypothesis was abandoned. C. Winkler, however, considers that the difficulties with the



above-cited investigators were due to impurities derived from the glass vessels, and was unable to confirm their results. Hence he concludes: "I cannot believe that nickel contains a hitherto unknown substance differing in properties and atomic weight; on the contrary, I consider both nickel and cobalt to be simple substances, and elements in the present sense of the word." C. Zimmermann, H. Remmler, P. Schützenberger, R. Vogel, and A. Sakoschansky discussed the place of cobalt in the periodic system. F. H. Parker and F. P. Sexton stated that in some electrolytic comparisons of cobalt and silver, they obtained 57.7 as a mean value for the at. wt. of cobalt, which is lower than that of nickel. The atomic numbers by H. G. J. Moseley, the lattice constants of T. Barth and G. Lunde, the m.p., and the cathode and anodic polarizations of R. Schilb, all agree with a position for cobalt between iron and nickel; F. K. Richtmyer and F. W. Warburton, J. J. Thomson, and C. G. Barkla and C. A. Sadler found that the permeability of metals for the X-rays is a periodic function of the at. wts. of the elements, and by interpolation, they obtained 61.2 to 61.6 for the at. wt. of nickel. S. Meyer, and O. Liebknecht and H. du Bois concluded that the at. wt. of cobalt is less than that of nickel because of its paramagnetic properties. These conclusions, said F. W. Clarke, "cannot weigh very heavily against the clear chemical evidence" of the misfit in the periodic table—1. 6, 5.

In 1857, E. R. Schneider determined the carbon dioxide evolved during the ignition of the oxalate, and from the ratio  $\text{Co} : 2\text{CO}_2 = 100 : 146.665$ , obtained 60.05 for the at. wt. of cobalt and about 58 for that of nickel. J. C. G. de Marignac, in 1858, found, in opposition to E. R. Schneider, that the at. wts. of cobalt and nickel are nearly the same. By calcining the sulphate to oxide, he obtained  $\text{CoSO}_4 : \text{CoO} = 100 : 48.287$ , or 58.761 for the at. wt. of cobalt; and by analyzing cobalt chloride for chlorine, by titration with silver nitrate, he obtained  $2\text{Ag} : \text{CoCl}_2 = 100 : 60.118$ , or 58.797 for the at. wt. J. B. Dumas' analyses of cobalt chloride gave 59.034 for the at. wt.; and C. Winkler's, 59.776. C. Winkler analyzed cobalt chloride gravimetrically, and from the ratio  $2\text{AgCl} : \text{Co} = 100 : 20.864$ , calculated 59.812 for the at. wt. W. Hempel and H. Thiele likewise obtained 58.929; by the synthesis of the chloride they obtained from the ratio  $\text{Cl}_2 : \text{Co} = 100 : 82.873$ , and the at. wt. 58.769; and by the synthesis of the iodide, they calculated from the ratio  $\text{I}_2 : \text{Co} = 100 : 23.462$ , the at. wt. 59.556. T. W. Richards and G. P. Baxter obtained from the synthesis of the chloride,  $\text{Cl}_2 : \text{Co} : 100 : 83.266$ , or 59.047 for the at. wt.; from the ratio  $2\text{Ag} : \text{CoBr}_2 = 100 : 101.407$ ,  $\text{Co} = 58.964$ ; from  $2\text{AgBr}_2 : \text{CoBr}_2 = 100 : 58.255$ , or  $\text{Co} = 58.969$ ; and from  $\text{CoBr}_2 : \text{Co} = 100 : 26.952$ ,  $\text{Co} = 58.972$ . G. P. Baxter and F. B. Coffin obtained  $2\text{Ag} : \text{CoCl}_2 = 100 : 60.1975$ , or  $\text{Co} = 58.968$ ; and  $2\text{AgCl} : \text{CoCl}_2 = 100 : 45.3070$ , or  $\text{Co} = 58.969$ .

W. J. Russell dissolved the metal in hydrochloric acid, and measured the hydrogen evolved, and from the ratio  $\text{Co} : \text{H}_2 = 100 : 3.4112$ , he calculated  $\text{Co} = 59.077$ . W. J. Russell also reduced cobaltous oxide by heating it in hydrogen, and from the ratio  $\text{CoO} : \text{Co} = 100 : 78.592$ , he calculated  $\text{Co} = 58.738$ . C. Zimmermann likewise obtained  $\text{Co} = 58.889$ ; H. Remmler, 59.812; W. Hempel and H. Thiele, 58.769; and T. W. Richards and G. P. Baxter, 58.973. C. Winkler measured the gold precipitated by cobalt from soln. of sodium chloroaurate, and from the ratio  $2\text{Au} : 3\text{Co} = 100 : 45.172$ , calculated  $\text{Co} = 59.386$ .

E. von Sommaruga analyzed the pentamminochloride, and obtained from the ratio  $\text{Co}(\text{NH}_3)_5\text{Cl}_3 : \text{Co} = 100 : 23.827$ , the at. wt.  $\text{Co} = 59.909$ ; R. H. Lee likewise obtained  $\text{Co} = 59.095$ . P. Weselsky analyzed ammonium cobaltcyanide, and calculated from the ratio  $(\text{NH}_4)_3\text{CoCy}_6 : \text{Co} = 100 : 21.943$ , the at. wt.  $\text{Co} = 59.085$ ; and similarly with phenylammonium cobaltcyanide, obtained the ratio  $(\text{C}_6\text{H}_5\text{NH}_2)_3\text{CoCy}_6 : \text{Co} = 100 : 11.8665$ , from which he calculated the at. wt.  $\text{Co} = 59.017$ . R. H. Lee obtained from brucine cobaltcyanide,  $(\text{C}_{23}\text{H}_{26}\text{N}_2\text{O}_4)_3\text{H}_3\text{CoCy}_6 \cdot 10\text{H}_2\text{O} : \text{Co} = 100 : 3.7437$ , or  $\text{Co} = 59.1991$ ; and from strychnine cobaltcyanide,  $(\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_2)_3\text{H}_3\text{CoCy}_6 \cdot 4\text{H}_2\text{O} : \text{Co} = 100 : 4.5705$ , or  $\text{Co} = 59.096$ .

From the results available in 1910, F. W. Clarke calculated for the best representative value 58.961. G. P. Baxter and co-workers obtained 58.940 for the best representative value of terrestrial cobalt, and 58.942 for meteoric cobalt. The results of T. W. Richards and co-workers give 58.97 for the at. wt. of cobalt, and 58.94 is the value adopted by the International Committee for 1931. The at. wts. of the family of elements was discussed by G. D. Hinrichs, and M. Gerber.

The **atomic number** of cobalt is 27, when that of iron is 26, and that of nickel 28. P. Vinassa<sup>3</sup> studied the molecular numbers of cobalt compounds; and D. de Barros, the nuclear numbers. F. Sanford discussed the relations between the atomic numbers and the physical and chemical properties of the elements; A. F. Scott, between the numbers and the ionic properties in the crystal lattice; and M. Kahanovicz, between the atomic numbers and the elastic constants. According to F. W. Aston, there are no **isotopes**, since only one kind of atom of mass 59 has been observed, although A. S. Russell anticipated an isotope of mass 57 from his study of the isotopes of radioactive and non-radioactive elements. T. R. Bull and S. S. Cooper studied the isotopes of cobalt. E. Rutherford and J. Chadwick, and J. D. Cockroft and E. T. S. Walton have not reported any definite evidence of **atomic disruption** by the bombardment of cobalt with  $\alpha$ -particles, although H. Pettersson and G. Kirsch said that there is evidence of a slight disruption of the atom.

N. Bohr, and E. C. Stoner represented the **electronic structure** of the atom on the assumption that the electrons present are (2) for the K-shell; (2, 2, 4) for the L-shell; (2, 2, 4, 3, 4) for the M-shell; and (2) for the N-shell. The electronic structure was discussed by C. M. Blackburn, H. Collins, O. Feussner, P. D. Foote, H. Grimm, W. D. Harkins, W. Kimura, R. Ladenburg, A. E. Lacomblé, H. Lessheim and co-workers, G. N. Lewis, L. W. McKeegan, S. Meyer, P. Niggli, C. D. Niven, H. Perlitz, N. S. Grace, G. I. Pokrowsky, P. R. Ray, W. H. Rothery, A. S. Russell, M. N. Saha, M. N. Saha and B. B. Ray, R. Samuel and E. Markowicz, J. D. M. Smith, A. Sommerfeld, R. Sonder, D. Strömholm, R. Swinne, A. T. Williams, H. J. Walke, E. Fermi, P. D. Foote, H. Kopfermann and E. Rasmussen, and L. Zehnder. The electronic structure of complex salts was discussed by D. M. Bose, C. J. Brockman, B. Cabrera, R. H. Fowler, M. L. Huggins, L. C. Jackson, H. Lessheim and co-workers, T. M. Lowry, C. D. Nenitzesco, P. R. Ray, N. V. Sidgwick, C. H. Spiers, P. Weiss, and L. A. Welo and O. Baudisch; the relation between the fusibility and electronic structure, by P. Vinassa; between the heat of dissolution and the valency electrons, by A. F. Richter; the energy of the electronic combination, by E. A. Milne; the relation between the electronic structure and electrical conductivity, by L. Bloch, D. P. R. Chaudhury, J. C. McLennan and co-workers, J. W. Nicholson, and M. N. Saha and B. B. Ray; the electron structure and the passive state, by A. S. Russell and co-workers, and R. Swinne; and the relation between the electron structure and magnetization, by D. M. Bose, B. Cabrera, J. Dorfman and R. Jaanus, M. L. Huggins, L. C. Jackson, R. Ladenburg, H. Lessheim and co-workers, L. W. McKeegan, P. R. Ray, A. Sommerfeld, R. Swinne, P. Weiss, and L. A. Welo and O. Baudisch.

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### § 9. Intermetallic Compounds or Alloys of Cobalt

According to G. Guillemin,<sup>1</sup> **copper-cobalt alloys** are readily obtained by melting the two metals together under a flux of boric acid and wood-charcoal, or by melting copper with an alloy of copper and cobalt formed in the process of copper smelting. N. S. Konstantinoff melted the mixed metals in a magnesia crucible in an electric furnace in an atm. of hydrogen or nitrogen; and R. Sahmen melted them in a porcelain tube in an atm. of dry hydrogen. J. Jahn reduced the mixed oxides by hydrogen, and also by aluminium in the thermite process. D. S. Ashbrook found that copper mixed with cobalt is deposited electrolytically from an electrolyte containing 0.25 grm. of metal per 1 c.c. of conc. sulphuric acid, or 10 c.c. of phosphoric acid of sp. gr. 1.085, and 50 c.c. of a 10 per cent. soln. of sodium hydrophosphate, using a rotating anode. The observations of W. Guertler, L. Guillet, N. S. Konstantinoff, A. Neuburger, F. Ducelliez, and R. Sahmen give no indication of the formation of definite chemical compounds, but give either homogeneous solid soln., or two-phase systems of solid soln. G. Tammann and W. Oelsen observed that the solubility,  $S$  per cent., of cobalt in copper can be represented by  $\log S = -2269T^{-1} + 2.343$ , and they found by extrapolation at 20°,  $S = 0.054$ , and that at :

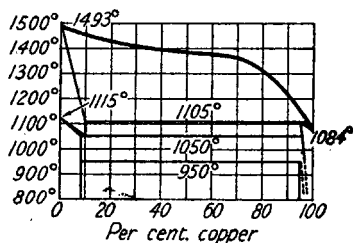


FIG. 35.—Freezing-point Curves of the System: Copper-Cobalt.

	1070°	985°	800°	690°	502°	442°
$S$ . . .	4.51	3.52	1.72	0.94	0.26	0.22

R. Sahmen's freezing-point curve is shown in Fig. 35. The metals form two series of solid soln. with 0 to 10 per cent. and 95.5 to 100 per cent. of copper respectively. There is a break in the cooling curve at 1100° with alloys having 10 to 95 per cent. of copper, below which the alloy solidifies completely to a conglomerate of two series of solid soln. On cooling, the  $\beta$ - or non-magnetic cobalt changes to the ordinary  $\alpha$ - or magnetic form. The transition temp. is lowered from 1115° for purified cobalt to 1050° by the addition of 10 per cent. of copper; it remains constant at 1050° for alloys, with up to 90 per cent. of copper; and then falls with the further addition of copper. Alloys with 99 per cent. of cobalt are still magnetic. N. S. Konstantinoff said that as cobalt is added to copper, the f.p. is raised so that the f.p. curve has four branches indicating the existence of solid soln. The break with 6.5 per cent. of cobalt represents a sat. soln. of cobalt in copper; and there

are also breaks corresponding with 30 and 70 per cent. of cobalt. The copper forms a solid soln. with up to 85 per cent. of cobalt; and alloys with 30 to 70 per cent. of cobalt form two layers in the liquid state. L. Vegard and H. Dale found that, unlike the alloys with nickel, those with cobalt form two series of solid soln. Alloys with 100, 75, 50, and 25 per cent. of copper have lattice constants respectively  $a=3.61$ ,  $3.60$ ,  $3.60$ , and  $3.60$  Å., and those with 50, 25, and 0 per cent. of copper they may have, respectively,  $a=3.539$ ,  $3.539$ , and  $3.533$  Å. R. Sahmen said that the maximum in the thermoelectric force with about 97 per cent. of copper, and W. Guertler, that the maximum in the electrical conductivity curve for about 95 per cent. copper, represent a sat. solid soln.

According to G. Guillemin, alloys containing 1 to 6 per cent. of cobalt have a red colour and a fine, silky fracture resembling that of copper. According to N. S. Kurnakoff and S. F. Schemtschuschny, the alloys may contain dendrites of cobalt. H. Behrens said that the alloys with 20 per cent. of copper have a fine-grained, crystalline structure, and when etched with 50 per cent. sulphuric acid they show a pale red, irregular network in a brownish-red matrix which also contains small, grey granules of an alloy rich in cobalt. L. Vegard and H. Dale found that the cubic lattice of cobalt is stabilized by copper. R. Sahmen observed that the fracture of alloys with over 15 per cent. of copper is red, and the hardness of the solid soln. rich in copper is 3, and that of solid soln. rich in cobalt is 4. M. Waehlert found Brinell's hardness of the alloys to be:

Copper	100	90	80	70	60	50	40	30	20	10 per cent.
Hardness	28	75	81	103	106	112	124	130	135	180

M. G. Corson, A. W. Smith, and C. S. Smith discussed the mechanical properties of the air-hardened alloys. A. Valenciennes said that the annealed alloys are ductile, and G. Guillemin observed that alloys with 1 to 6 per cent. of cobalt are remarkably ductile, malleable, and tenacious; they can be worked and rolled in the cold, but they cannot be tempered; they break under a tensile strain of 25 to 36 kgrms. per sq. mm., and have an elongation of 15 to 28 per cent. An alloy with 5 per cent. of cobalt, after forging and rolling, broke under a strain of 40 kgrms. per sq. mm. and had an elongation of 10 per cent. This alloy was as malleable and as little liable to oxidation as copper, and was as ductile and tenacious as iron.

The effect of small quantities of cobalt on the electrical properties of copper was found by G. Reichardt to be almost as great as that of manganese, and about three times as great as that of nickel. W. Guertler stated that there is a sharp break in the sp. electrical resistance curve of alloys with 5 vol. per cent. of cobalt. G. Reichardt observed that the sp. resistance of copper increases rapidly with additions of up to 3.2 per cent. of copper and attains 9.5 microhms per cm. cube. The results are indicated in Table II, where the sp. resistance is expressed in

TABLE II.—SOME PROPERTIES OF THE COBALT-COPPER ALLOYS.

Cobalt per cent.	R microhms	Temp. coeff.	Thermal e.m.f. $\times 10^6$	Cobalt per cent.	R microhms	Temp. coeff.	Thermal e.m.f. $\times 10^6$
0	1.672	0.004450	—	23.6	11.43	0.000817	26.5
1.5	6.76	0.001084	30.8	34.4	12.10	0.000936	25.9
1.9	8.80	0.000859	32.1	46.6	11.34	0.00132	20.8
3.1	9.45	0.000768	33.0	59.4	12.92	0.00143	19.4
4.1	9.45	0.000771	32.1	70.3	14.79	0.00150	18.5
5.1	8.63	0.000820	32.8	80.5	16.57	0.00166	17.6
6.7	10.02	0.000801	31.5	90.4	24.30	0.00167	16.7
13.9	10.72	0.000776	29.1	99.8	9.73	0.00326	26.8

microhms per cm. cube at 20°; then follows the temp. coeff. of the resistance; and finally, the thermal e.m.f. against copper is expressed in  $10^{-6}$  volt per degree.

The addition of 3 to 5 per cent. of cobalt gives an alloy with a minimum temp. coeff. of the resistance of 0.00077, and a maximum thermoelectric effect of 33 microvolts for 1 degree difference of temp. Up to this proportion of cobalt, the sp. resistance of the alloys increases rapidly, but a further addition of cobalt produces only a slow increase of resistance. The sp. resistance has a maxima with between 3 and 4 per cent., and about 34.4 per cent. of cobalt. The alloys can be used in making thermoelectric couples. All the cobalt-copper alloys, except those containing less than 1.5 per cent. of cobalt, can be magnetized, and the magnetism is destroyed only at a red-heat. W. Broniewsky discussed the thermoelectric force.

R. Sahmen observed that the magnetism disappears at 1115° with 100 per cent. cobalt, Fig. 35; at 1050°, with 10 per cent. copper, and it then remains constant for alloys with up to 90 per cent. copper; it falls to 950° for alloys with 95 per cent. copper, and thereafter falls rapidly. G. Tammann and W. Oelsen measured the specific magnetization (gauss) of copper-cobalt alloys containing the following proportions of dissolved and total cobalt:

		1070°	1010°	890°	690°	392°	20°
Dissolved Co	.	4.51	3.75	2.51	0.94	0.22	0.220
Gauss	{ 0.50 per cent. Co	0.01	0.002	0.001	0.002	0.390	0.390
	{ 1.00 " Co	0.002	0.004	0.003	0.128	1.230	1.23
	{ 5.00 " Co	0.698	1.68	3.98	6.44	7.33	7.34
	{ 22.5 " Co	26.6	27.0	30.2	32.9	33.8	33.7

G. Tammann observed that the temp. of the magnetic transformation of cobalt is lowered 30° by the addition of 5.2 per cent. of copper; and he suggested that the magnetizability of the alloys rich in copper is conditioned by the presence of crystals of a solid soln. rich in cobalt. A. Kussmann and B. Scharnoff studied the coercive force of the alloys.

W. Guertler and T. Liepus found that a 10 per cent. soln. of sodium hydroxide had no attack on the 1:1-alloy in 8 hrs., but with a 15 per cent. soln. the metal was attacked. The alloy was also attacked in 8 hrs. by 10 and 50 per cent. nitric acid; by 10 and 36 per cent. hydrochloric acid; aqua regia; 10 per cent. sulphuric acid; 20 per cent. sulphuric acid sat. with sodium sulphate; sodium hydroxide and hydrogen dioxide, 10, 50, and 70 per cent. aq. ammonia; 10 and 50 per cent. sodium sulphide, and 4 per cent. sodium sulphide mixed with 8 per cent. of alkali; chlorine water; sea-water; sea-water plus air; rain-water and air; and a soln. of magnesium chloride. A 1:500-soln. of mercuric chloride was not stable in contact with the alloy. According to M. Waehlert, the losses in mgrms. per sq. mm. of the alloys when exposed to nitric and sulphuric acids of different concentration, in percentages, for the time in hours stated in brackets, are:

Copper	90	80	70	60	50	40	30	20	10%
HNO <sub>3</sub>	{ 1 (48)	0.67	0.42	0.36	0.42	0.60	0.65	—	—
	{ 5 (24)	0.25	3.35	2.10	2.10	0.95	0.84	—	—
	{ 10 (24)	10.50	13.30	3.65	4.00	1.78	1.30	—	—
	{ 20 (24)	380.00	16.40	4.60	1.20	0.51	0.34	—	—
	{ 30 (24)	—	92.50	16.30	1.17	0.34	0.34	—	—
	{ 50 (24)	—	—	693.50	46.20	19.50	9.98	—	—
H <sub>2</sub> SO <sub>4</sub>	{ 1 (72)	—	—	—	0.25	—	—	0.51	—
	{ 5 (72)	0.17	0.17	0.17	0.17	0.08	—	0.17	0.25
	{ 10 (24)	0.25	0.59	1.85	0.42	0.60	1.10	0.43	0.34
	{ 20 (24)	0.08	—	—	—	0.07	—	0.17	—
	{ 30 (24)	0.17	—	—	—	0.07	—	—	—
	{ 50 (24)	0.08	—	—	—	0.07	—	—	—

According to G. J. Petrenko,<sup>2</sup> **cobalt-silver alloys** cannot be prepared below 1600°, for up to this temp. the two elements are completely insoluble in one another. K. Masaki prepared alloys by electrodeposition. E. Pannain said that if alloyed with a third metal, silver and cobalt furnish alloys containing the three metals in various proportions; F. Ducelliez found silver to be insoluble in cobalt, so that when the two metals are melted together, say 95 per cent. of silver, on cooling virtually

pure silver separates out, and a metal containing 80.77 per cent. of silver. When an ingot with 70.25 per cent. of silver is liquated, at a temp. between the m.p. of the two metals, pure silver was obtained, and the lower part of the ingot became richer in silver. No evidence of a eutectic was observed; and G. J. Petrenko found that the two breaks in the cooling curve corresponded respectively with the m.p. of cobalt and of silver. W. Oelsen found that silver dissolved  $5.5 \times 10^{-4}$  per cent. of cobalt. According to F. Ducelliez, after etching the alloys with hydrochloric acid, the surfaces showed (i) grey zones, often elongated, and rich in silver; and (ii) bright zones corresponding with silver. With  $N\text{-CoSO}_4$ , the alloys gave no e.m.f. with cobalt poles, but gave a constant e.m.f. of 0.535 volt with silver poles. All the alloys were magnetic; and all were attacked by hydrochloric acid—those rich in cobalt leaving silver powder; those moderately rich in cobalt giving lamellæ of silver; whilst those poor in cobalt retained their shape, but became brittle, and after treatment with acid, they could be broken up by a hammer.

C. Hatchett<sup>3</sup> found that the dark yellow **cobalt-gold alloy**, with 18 parts of gold and 1 part of cobalt, is brittle and possesses a pale yellow fracture; an alloy

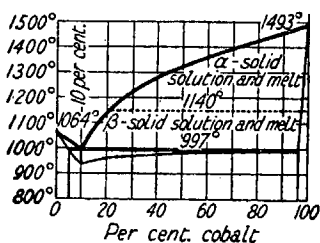


FIG. 36.—Freezing-point Curves of Cobalt-Gold Alloys.

with  $\frac{1}{65}$ th of cobalt is brittle, but with  $\frac{1}{115}$ th of cobalt is malleable. Alloys were also prepared by Richter and Co., and E. Jänecke. According to W. A. Wahl, molten cobalt and gold can be mixed in all proportions. The alloys show the same phenomena on melting as those shown by cobalt alone—*vide supra*. The f.p. curves, Fig. 36, have two branches meeting at a eutectic at 997° and 72.9 at. per cent., or 90 per cent. of gold. Solid soln. containing 0 to 5.5 per cent., and 96.5 to 100 per cent. of cobalt are formed. The crystals rich in cobalt must be cubic above 1140°, being isomorphous with  $\beta$ -cobalt; and hexagonal below that temp., corresponding with  $\alpha$ -cobalt. All the alloys are magnetic, and the magnetizability falls with increasing proportions of gold, rapidly at first, and then more slowly; it increases with the temp., being three times as great at the eutectic temp. as in the cold. J. O. Linde studied the electrical resistance of the alloy; and G. Borelius and co-workers, the thermoelectric properties.

H. N. Warren<sup>4</sup> prepared a **calcium-cobalt alloy** by reducing cobalt oxide with calcium carbide; and M. Tarugi, by reducing cobalt salts with the same reagent. G. Masing, and W. Hessenbruch, prepared **beryllium-cobalt alloys**. The cementation of cobalt with beryllium was studied by I. Fetchenko-Tchopivsky, who found that beryllium is insoluble in cobalt below 1300°. G. Masing and O. Dahl said that beryllium is sparingly soluble in cobalt at a high temp., and even less soluble on a falling temp. The hardness and tensile properties may be increased by quenching and ageing at suitable temp.

J. Parkinson<sup>5</sup> could not obtain **magnesium-cobalt alloys** by melting a mixture of the component metals. A. F. Gehlen prepared a grey **cobalt-zinc alloy** with a metallic lustre by heating a mixture of cobalt and zinc turnings (1 : 2). C. Gourdon, B. Egeberg, and F. Ducelliez also obtained an alloy of the two metals. Alloys were obtained by simultaneous electrodeposition from aq. soln. of the component salts by R. Kremann and co-workers, by R. Müller and F. R. Thoïs, and by S. Glasstone. K. Lewkonja obtained crystals of solid soln. with proportions of cobalt ranging from 0.5 to 18.5 per cent. The sat. solid soln. contains 13.4 per cent. of cobalt. The eutectic, according to K. Lewkonja, is 5° below the m.p. of zinc, and, according to W. M. Peirce, 1° below the m.p. There is evidence, Fig. 37, of the formation of a non-magnetic **cobalt tetrazincide**,  $\text{CoZn}_4$ . The subject was studied by N. Parravano and V. Caglioti, and L. Guillet; and A. R. Russell and co-workers studied the compounds formed in mercury soln. A. Westgren studied the X-radiogram of the **cobalt pentitadizincide**,  $\text{Co}_5\text{Zn}_2$ , and also the

relation between the crystal structure and atomic properties of the cobalt-zinc alloys. A. J. Bradley, and W. Ekman studied the X-radiograms, and they preferred the formula  $\text{Co}_5\text{Zn}_2$  to  $\text{CoZn}_4$ . F. Ducelliez also obtained the alloy by melting zinc with 18.46 per cent. of cobalt. The sp. gr. is 7.43 at  $0^\circ$  when the calculated value is 7.11. The e.m.f. of the cell  $\text{Zn} : \text{N} - \text{ZnSO}_4 : \text{Co}_n\text{Zn}_m$  decreases slowly with increasing cobalt up to 20 per cent. cobalt, and it then rises very rapidly. The cell  $\text{Co} : \text{N} - \text{ZnSO}_4 : \text{Co}_n\text{Zn}_m$  behaves similarly. The break in the e.m.f. curve is supposed to correspond with the tetrazincide. S. Glasstone found the deposition potentials of cobalt and zinc from soln. of the two sulphates. K. Lewkonja said that alloys with no more than 20 per cent. of cobalt are not ferromagnetic; and F. Ducelliez, that alloys rich in cobalt are ferromagnetic. When the tetrazincide is heated in hydrogen, the zinc evaporates. The powdered alloy oxidizes quickly in air at ordinary temp., and it burns at a red-heat in air, or in contact with molten potassium chlorate. It is attacked by boiling water. It is attacked by chlorine at a dull red-heat with incandescence. One per cent. hydrochloric acid attacks the tetrazincide in the cold; and alloys with over 83 per cent. of zinc leave finely-divided cobalt as a residue when treated with boiling dil. acid, and with cold, 1 per cent. hydrochloric acid a residue of the tetrazincide remains, and with alloys having 11.7 to 78 per cent. of zinc, the residue has approximately the same composition as the original alloy—similarly also with 1 per cent. nitric acid. The tetrazincide reacts vigorously with liquid or the vapour of sulphur; it is attacked by cold, 1 per cent. sulphuric acid, and 1 per cent. nitric acid; it is attacked by molten alkali hydroxides, carbonates, or nitrates. Soln. of cobalt sulphate or chloride dissolve zinc from the tetrazincide—particularly with hot soln.—and leave a ferromagnetic residue, but the zinc is not dissolved by soln. of cobalt nitrate. J. Jahn found that the **cobalt-zinc-copper alloys**, or cobalt brasses, analogous to nickel-silver (*q.v.*), with cobalt in place of nickel, are silver-white, brittle, and hard. The alloys are attacked rather more when heated with hydrogen sulphide, and sulphur dioxide than is the case with the nickel silvers. Observations were made by L. Guillet, D. Iitsuka, and W. M. Peirce. C. Browne observed that the addition of cobalt to 80:20-copper-zinc alloy raised the tensile strength considerably. Thus, with wires 0.7 mm. in diameter:

Cobalt . . . . .	0	0.12	0.21	0.50 per cent.
Tensile strength . . . . .	26.1	28.0	29.9	31.2
Percentage increase . . . . .	—	9.2	14.6	19.6 per cent.

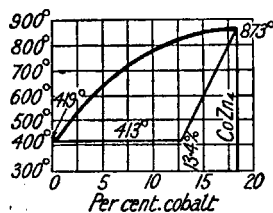


FIG. 37.—Freezing-point Curves of Zinc-Cobalt Alloys.

K. Lewkonja also prepared some **cobalt-cadmium alloys**. He found that the f.p. of cadmium is lowered  $6^\circ$  by the addition of cobalt, and the eutectic furnishes a mass containing crystals which are either a compound of the two elements, or else crystals of a solid soln. sat. with cadmium, because the alloys with up to 10 per cent. of cobalt are non-magnetic at room temp. A. S. Russell and co-workers observed that no compounds are formed in mercury soln. R. Kremann and co-workers, and R. Müller and F. R. Thois prepared alloys by electrodeposition.

R. Böttger,<sup>6</sup> C. F. Schönbein, J. Schumann, and H. Moissan prepared **cobalt-mercury alloys**, or **cobalt amalgams**, from sodium amalgam and a conc. soln. of cobalt chloride, at the same time the liquid becomes violet owing to the separation of cobaltous hydroxide. W. Kettembeil also prepared cobalt amalgam by the action of potassium amalgam in soln. of cobaltous chloride sulphate, or nitrate. A. A. Damour immersed zinc amalgam—1 part of zinc and 6 parts of mercury—in an aq. soln. of cobaltous chloride, sat. with ammonia. Hydrogen is evolved. The liquid over the amalgam is renewed as often as it loses its colour. The zinc in the cobalt amalgam can be extracted by boiling dil. sulphuric acid, which does



not act on the cobalt amalgam. Aq. soln. of cobaltous sulphate or chloride do not act so quickly as the ammoniacal soln. of the chloride, and aq. soln. of cobalt nitrate give nothing but hydrated cobaltous oxide. P. Casamajor obtained cobalt amalgam by the process used for iron amalgam (*q.v.*), that is, by shaking up cobalt with sodium amalgam and dil. acid. H. Moissan, and J. Schumann prepared the amalgam by electrolyzing a soln. of cobaltous chloride with a platinum anode, and a mercury cathode; H. Nagaoka similarly electrolyzed a soln. of cobaltic chloropentamminochloride; L. Paraskovich, and R. Erban and L. Paraskovich, a soln. of ammonium cobaltous sulphate and boric acid; and A. S. Russell and co-workers, a soln. of cobaltous sulphate in  $4N\text{-H}_2\text{SO}_4$ . G. Tammann and co-workers gave  $1.7 \times 10^{-1}$ , and N. M. Irvin and A. S. Russell,  $< 8 \times 10^{-5}$  grm. per 100 grms. of mercury for the solubility of cobalt. J. Schumann prepared an amalgam electrolytically corresponding with  $\text{Hg}_{10}\text{Co}_3$ .

According to R. Böttger, the amalgam is less fluid than mercury, and is not affected by a magnet until a part of the mercury has been driven off by heat. J. Schumann found that the amalgam prepared by R. Böttger's process contains, besides the silver-white liquid amalgam, hard crystals of a darker colour. R. Böttger found that when the amalgam is heated, there remains a black residue of cobalt and its oxide. A. A. Damour said that when the amalgam is heated in a closed vessel, the mercury is given off, leaving the cobalt in the form of a grey, metallic mass—*vide supra*, pyrophoric cobalt. G. Tammann and K. Kollmann found that the e.m.f. of the cell,  $\text{HgCo}_m : 2N\text{-CoSO}_4 : \text{HgCl}$ , Hg falls at first rapidly, and after a few hours furnishes an e.m.f. corresponding with that of the saturated amalgam. J. Schumann observed that the liquid amalgam is less magnetic the more mercury it contains. J. Schumann, and A. A. Damour said that the amalgam is a dull silver-white colour, and is attracted by a magnet. H. Nagaoka studied the magnetic properties of the amalgam, and G. Tammann and W. Oelsen found that for an amalgam with 0.062 per cent. cobalt, the sp. magnetization is 0.311 gauss. A. A. Damour said that when cobalt amalgam is exposed to air, it becomes covered with a black powder of oxidized cobalt; but J. Schumann found the dark-coloured, hard crystals are not changed by exposure to air, and although the liquid amalgam is stable out of contact with air, it decomposes on exposure to air for 24 hrs. into a black powder of oxidized cobalt, and mercury. H. Nagaoka said that an amalgam with 5 per cent. of cobalt oxidizes readily in air, but it is protected from oxidation by a covering layer of boiled linseed oil. L. Paraskovich, and R. Erban and L. Paraskovich observed very little oxidation when amalgams with 0.2 to 0.5 per cent. of cobalt are exposed to air for a year. C. F. Schönbein found that when cobalt amalgam is shaken with water, or, better, with dil. sulphuric acid, some hydrogen dioxide is formed. J. Schumann observed that the amalgam is slowly decomposed by water, and it is insoluble in mercury. H. Moissan found that water without air forms cobaltous hydroxide, and with air a black, higher oxide. A. S. Russell and co-workers studied the order of removal of the metals from amalgams by oxidizing agents—ferric sulphate, potassium permanganate, and uranyl sulphate—and obtained the order Zn, Mn, Cu, Cr, Fe, Mo, Co, Hg, Ni, and W. M. Rabinovich and P. B. Zywtinsky found that cobalt is dispersed in mercury above the solubility limit to form a colloidal soln. G. Michaud reported a **cobalt-ammonium-mercury alloy**; and J. Schumann, a **cobalt-zinc-mercury alloy**.

I. Fetchenko-Tschopivsky<sup>7</sup> studied the **cobalt-boron alloys** produced by cementation. C. Margot prepared **aluminium-cobalt alloys**, with 75 to 80 per cent. of cobalt, by melting a mixture of the component metals at a bright red-heat. The alloys were crystalline, brittle, and of the hardness of steel. They disintegrated after some days into a violet powder. Some alloys were also prepared by L. Guillet, S. Daniels, W. Pruszkowsky, H. Bohner, and N. Parravano and P. Agostini. H. Schirmeister said that the crucibles employed for making the alloys should be free from sulphur and carbon, since these substances make the alloys worthless.

A. G. C. Gwyer measured the f.p. of the alloys, and the curves, Fig. 38, have a maximum at  $1628^{\circ}$  and 68.5 per cent. of cobalt, corresponding with **cobalt aluminide**,  $\text{CoAl}$ ; and two breaks at  $1165^{\circ}$  and 38 per cent. of cobalt, and at  $940^{\circ}$  and 20 per cent. of cobalt. There is a minimum in the curve at  $1375^{\circ}$  and 90.5 per cent. of cobalt. There are two series of solid soln. containing respectively 68.5 to 80 per cent. and 90.5 to 100 per cent. of cobalt. The alloys with 82 to 90 per cent. of cobalt do not become homogeneous when heated for 3 hrs. at  $1250^{\circ}$  to  $1270^{\circ}$ . At  $1165^{\circ}$ , the cobalt monoaluminide reacts with the fused mass to form **cobalt hemipentaluminide**,  $\text{Co}_2\text{Al}_5$ ; and at  $940^{\circ}$  to form **cobalt tritridecaluminide**,  $\text{Co}_3\text{Al}_{13}$ . W. L. Fink and H. R. Freche found crystals of **cobalt hemiennaluminide**,  $\text{Co}_2\text{Al}_9$ . The hypoeutectic liquidus is a straight line extending from the f.p. of aluminium to the eutectic. Less than 0.02 per cent. of cobalt dissolves in solid aluminium at  $655^{\circ}$ . The intersection of the hypereutectic liquidus with the eutectic horizontal occurs with 1 per cent. of cobalt. The diagram was also studied by L. Guillet, who supposed that the compounds  $\text{Co}_3\text{Al}$ ,  $\text{Co}_4\text{Al}$ ,  $\text{Co}_2\text{Al}$ ,  $\text{CoAl}_2$ , and  $\text{CoAl}_4$  can exist. S. Daniels said that the first eutectic lies between 0.40 and 0.94 per cent. of cobalt. The subject was investigated by W. L. Fink and H. R. Freche, who found that the solid solubility of cobalt in aluminium at  $655^{\circ}$  is less than 0.02 per cent.

O. Brunck obtained the 3 : 13-compound in parallel lamellæ which, when etched, form feathery crystals. A. J. Bradley, and A. Westgren discussed the structure of the cobalt aluminides. H. Schirmeister observed that alloys with 9 to 12 per cent. of cobalt had the best mechanical properties, although the tensile strength was very little greater than that of aluminium. Thus, the tensile strength in kgrms. per sq. mm., the percentage elongation, and Brinell's hardness of :

Cobalt	0	0.6	1.6	3.5	5.5	7.5	9.5	12.0 per cent.
Tensile strength	10.5	10.5	12.0	12.9	15.5	16.6	16.5	18.5
Elongation	34	35	28	21	18	14	11	6
Hardness	29	32	—	47	—	50	51	61

C. Margot said that alloys with 75 to 80 per cent. of cobalt are brittle, and as hard as hardened steel; and L. Guillet, that the sp. gr. of alloys with 5.4, 18.6, and 47.7 per cent. of aluminium have the sp. gr. 7.65, 5.87, and 4.15 respectively when the calculated values are 7.52, 5.93, and 4.05. W. Biltz and W. Holverscheit gave for the sp. gr. of  $\text{CoAl}$ , 6.03 at  $25^{\circ}/4^{\circ}$ , and the mol. vol. 14.3; and for  $\text{Co}_2\text{Al}_5$ , the sp. gr. 4.19 at  $25^{\circ}/4^{\circ}$ , and the mol. vol. 60.4; they gave for the heat of formation, 32 Cals. for  $\text{CoAl}$ , and 86 Cals. for  $\text{Co}_2\text{Al}_5$ . A. G. C. Gwyer gave  $1628^{\circ}$  for the m.p. of  $\text{CoAl}$ ; and found that  $\text{Co}_2\text{Al}_5$  has a transformation point at  $1100^{\circ}$ , and at  $1615^{\circ}$  decomposes into  $\text{CoAl}$ , and a melt; whilst at  $940^{\circ}$ ,  $\text{Co}_3\text{Al}_{13}$  decomposes into  $\text{Co}_2\text{Al}_5$ , and a melt. G. Tammann and K. Dahl said that the plastic deformation of  $\text{Co}_3\text{Al}_{13}$  begins at  $800^{\circ}$ . W. Borchers and K. Schirmeister improved the mechanical properties of these alloys by the addition of up to about 1.2 per cent. of tungsten or molybdenum. E. Morlet examined the effect of cobalt on the hardness of the copper aluminium alloys. According to A. G. C. Gwyer, only alloys with over 68.5 per cent. of cobalt are magnetic, and the temp. at which the magnetism disappears on heating is progressively lowered by aluminium, as indicated by the dotted line in Fig. 38. A. von Zeerleder studied the action of acids on the alloys. S. F. Herman and F. T. Sisco, and W. W. Stiefler studied the magnetic properties of some alloys. E. Morlet studied some **copper-aluminium-cobalt alloys**.

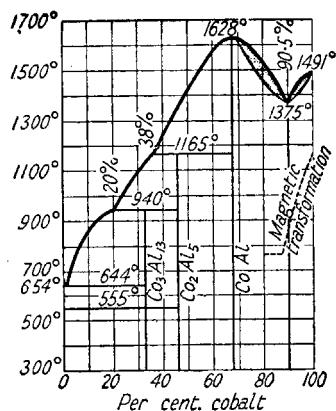


FIG. 38.—Freezing-points of the Aluminium-Cobalt Alloys.

K. Lewkonja prepared some **cobalt-thallium alloys**, but found that the two elements are only slightly miscible in the liquid and solid states. There is no evidence of the formation of definite compounds. The f.p. of thallium is lowered  $4^\circ$  by 2.5 per cent. of cobalt, and  $6^\circ$  by 2.87 per cent., and the transformation temp. is lowered  $7^\circ$  or  $8^\circ$ . Just over the m.p. of thallium only 2.5 to 3 per cent. of cobalt is dissolved, and in molten cobalt, only 2.87 per cent. of thallium dissolves; the remainder distills off.

M. Dubowicky, R. Walter, C. L. Wilson and co-workers, and A. M. Portevin studied the cobalt-silicon alloys, and the cementation of cobalt by silicon. B. Egeberg prepared **cobalt-titanium alloys** by the aluminothermic process, and found that the solubility of titanium with cobalt is about 3.5 per cent. titanium, and that the eutectic has 19 per cent. titanium. The tensile strength attains a maximum with 4.5 per cent. of titanium and 70 kgrms. per sq. mm.; Brinell's hardness rises steadily to 484 at 21.5 per cent. titanium. The thermal, electric, and magnetic properties were also examined. The resistance of the alloys to 5 per cent. nitric acid decreased almost to zero with 12 per cent. of titanium—6.40, 13. M. G. Corson, and C. W. Wilson and co-workers studied the **copper-cobalt-silicon alloys**. C. A. Winkler, A. J. Kieser, and E. Vigouroux studied the ternary system involving **silicon-aluminium-cobalt alloys**. A. Stavenhagen and E. Schuchard<sup>8</sup> obtained titanium-cobalt alloys by the thermite process. B. Egeberg made alloys with up to 20 per cent. of titanium and 2 to 3 per cent. of aluminium by the aluminothermite process. Alloys with 10 per cent. of titanium are coloured like cobalt, and those with higher proportions are silver-white. The hardness increases as the proportion of titanium rises from 0.5 to 11.0 per cent. The tensile strength increases rapidly with the titanium content up to a maximum of 70 kgrms. per sq. mm. with 5 to 6 per cent. of titanium, and an elongation of 5 per cent. The alloys with the greatest tensile strength have the finest grain. The mean coeff. of thermal expansion between  $20^\circ$  and  $200^\circ$  changes irregularly with composition between 0.041017 and 0.041112. The magnetic induction increases with increasing proportions of titanium; the remanence is greater with alloys having a heterogeneous texture than those with solid soln. The rate of dissolution of polished samples in 25 per cent. sulphuric acid at  $20^\circ$  to  $97^\circ$ , increases with

increasing proportions of titanium; and with 5 per cent. nitric acid at  $97^\circ$ , the rate of dissolution decreases. A soln. of 5 per cent. nitric acid, and 2 per cent. sodium chloride at  $97^\circ$ , attacks alloys with 2.31 and 4.67 per cent. of titanium at about the same rate, but alloys with 6.58 and 10.86 per cent. of titanium are attacked more quickly.

A. F. Gehlen prepared a violet, ductile **cobalt-tin alloy**. F. Ducelliez also obtained alloys of cobalt and tin by melting tin with powdered cobalt in a magnesia crucible in an atm. of hydrogen. Q. Marino obtained alloys by electrodeposition from soln. of the cyanides of the component salts along with alkali borotartrate and alkali or ammonium formate. F. Ducelliez said that alloys with 0 to 57.65 per cent. of tin contained as solid phases cobalt and **cobalt tritdistannide**,  $\text{Co}_3\text{Sn}_2$ ; alloys with 57.65 and 66.76 per cent. of tin contain  $\text{Co}_3\text{Sn}_2$  and **cobalt stannide**,  $\text{CoSn}$ ; and alloys with 66.76, 85, and up to 100 per cent. of tin contain the monostannide and tin. K. Lewkonja

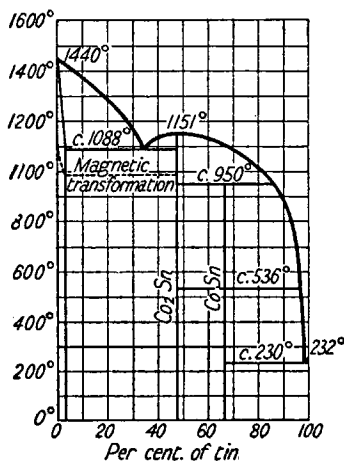


FIG. 39.—Freezing-point Curves of Cobalt-Tin Alloys.

obtained the f.p. curves shown in Fig. 39. The two elements are miscible in all proportions in the liquid state. In the solid state, the maximum amount of tin dissolved by cobalt is 3.5 per cent. The first eutectic is at about  $1088^\circ$ , and

the second eutectic at 229° or 230°. The f.p. curves show the existence of **cobalt hemistannide**,  $\text{Co}_2\text{Sn}$ , melting at 1151°; and of cobalt stannide,  $\text{CoSn}$ , which melts with decomposition at 943° or 950°. The monostannide undergoes a polymorphic change at about 536°. Alloys with 20 to 45 per cent. of tin have the same dark eutectic as those with less than 35 per cent. of tin, but in alloys with 35 per cent. of tin, the crystals of the hemistannide appear. Alloys with 50 per cent. of tin are cracked and fissured, and contain rounded polyhedra of the hemistannide with very little eutectic. Alloys with 50 to 85 per cent. of tin show the presence of the dark monostannide; and alloys with over 85 per cent. of tin show the primary separation of large needles of the monostannide surrounded by a eutectic of tin and the monostannide. S. F. Schemtschuschny and S. W. Belynsky confirmed these results and said that the maximum on the f.p. curve occurs at 1171°, and there is a transition point at 927°, whilst above 515°, the monostannide separates out in  $\alpha$ -crystals, and below in  $\beta$ -crystals. The eutectics were stated to occur at 229° and 79.5 at. per cent. of cobalt, and at 1112° with 1 at. per cent. of cobalt. The alloys were also studied by N. S. Konstantinoff. A. S. Russell and co-workers studied the system in mercury soln. G. Tammann and A. Rohmann found the heat capacity,  $c_{100}$  cal. per mol, for  $\text{Co}_2\text{Sn}$ , to be :

	-200° to -100°	-100° to 0°	0° to 100°	100° to 200°
$c_{100}$	1561.82	1739.30	1897.85	1968.85

P. Schübel gave for the true sp. ht.,  $c$ , of  $\text{Co}_2\text{Sn}$  :

	100°	200°	300°	400°	500°	600°
$c$	0.0824	0.0876	0.0900	0.0926	0.0944	0.0962

and H. Schimpff gave  $c=0.077873+0.04728544(\theta-17)-0.063033(\theta-17)^2$ , or for the true sp. ht.,  $c$ , and the at. ht.,  $C$  :

	-150°	-100°	-50°	0°	50°	100°
$c$	0.0572	0.0652	0.0716	0.0765	0.0800	—
$C$	13.30	15.29	—	18.04	—	19.48

According to F. Ducelliez, when the alloys with 80.89 to 92.91 per cent. of tin are powdered, boiled with 25 per cent. nitric acid, levigated to remove metastannic acid, fused with potassium hydroxide and washed successively with water, alcohol, and ether, the monostannide remains. This compound can be formed by heating a mixture of atomic proportions of the two elements in an atm. of hydrogen. Combination occurs with incandescence; the product has a sp. gr. of 8.950 at 0°. The alloy is brittle at ordinary temp., and, according to G. Tammann and K. Dahl, plastic deformation begins at about 800°. A. Koch studied the potential of the alloy in a Daniell cell. F. Ducelliez, K. Lewkonja, and S. F. Schemtschuschny and S. W. Belynsky found that the monostannide is not ferromagnetic at room temp. G. Tammann and A. Koch found that the alloy becomes matte and darkens in colour when exposed to air for 10 to 20 minutes. F. Ducelliez noted that at a red-heat, the monostannide is attacked by chlorine, oxygen, and sulphur vapour; it is completely dissolved by hydrochloric or sulphuric acid, but is not attacked by boiling, dil. nitric acid, and only slowly by conc. nitric acid. G. Tammann and co-workers observed that at 18°, the monostannide is attacked, with a feeble evolution of gas, by  $N\text{-H}_2\text{SO}_4$ , and  $N\text{-HCl}$ . F. Ducelliez noted that fused alkali hydroxides, carbonates, nitrates, or chlorates attack the monostannide slowly. G. Tammann and A. Koch found that the monostannide precipitates copper, silver, and mercury from soln. of salts of these metals.

F. Ducelliez's tritadistannide evidently corresponds with K. Lewkonja's hemistannide. This compound can be isolated by treating the alloys, with 8.76 to 57.25 per cent. of tin, with 15 per cent. nitric acid followed by potassium hydroxide soln. The alloys behave like mixtures of cobalt and the tritadistannide, and their fragility, and the proportion of contained compound increase with the percentage of tin. There is no evidence of a cobalt tritastannide. The tritadistannide appears

as a powder having no well-characterized, crystalline form. Its sp. gr. is 8.86, and, like all the alloys containing it, it is magnetic. Its chemical properties resemble those of the monostannide, but it is less readily attacked by hydrochloric acid, and more easily attacked by nitric acid than is the case with the monostannide.

F. Ducelliez observed that the alloy with 80.89 per cent. of tin is grey and brittle; that with 89.28 per cent. of tin has a reticulated surface and can be cut; that with 92.91 per cent. of tin has the appearance and malleability of tin. F. Ducelliez observed that the electrode potentials of the alloys in  $N\text{-CoSO}_4$  correspond with the existence of the monostannide. N. A. Puschin observed that the e.m.f. in millivolts of the  $\text{Sn} : N\text{-H}_2\text{SO}_4 : \text{SnCo}_n$ , and the  $\text{Sn} : N\text{-KOH} : \text{SnCo}_n$  cells are respectively :

$n$	.	.	20	40	45	49.6	52	53.1	60	80	100
$N\text{-H}_2\text{SO}_4$	.	.	8	4	29	114	200	214	294	179	142
$N\text{-KOH}$	.	.	6	17	31	46	435	405	345	280	360

There is a break in the curve with 50 at. per cent. of cobalt corresponding with the monostannide. There is no sign of F. Ducelliez's tritastannide. G. Tammann and A. Koch studied the e.m.f. of the alloys. S. F. Schemtschuschny and S. W. Belynsky observed that the hemistannide is magnetic whilst the monostannide is non-magnetic in both the  $\alpha$ - and  $\beta$ -forms. F. Ducelliez, and K. Lewkonja also observed that only alloys with over 50 per cent. of cobalt are magnetic at ordinary temp., and the intensity of the magnetization increases as the proportion of cobalt increases. The transformation temp. of alloys with from 2.5 to 50 per cent. of tin is  $985^\circ$ . O. Barth observed that alloys with only small proportions of one or other of the metals are more readily attacked by acids than is the case with the pure metals. An alloy with 60 per cent. of tin is highly resistant to acids, but is brittle and unworkable. E. A. Drysdale studied the corrodibility of these alloys. O. Barth examined some alloys containing carbon.

According to F. Ducelliez,<sup>9</sup> homogeneous **lead-cobalt alloys** can be obtained by subjecting mixtures of the two metals to hydraulic pressure, and then heating

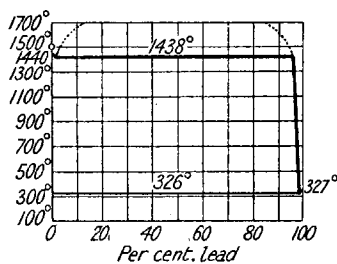


FIG. 40.—Freezing-point Curves of the Cobalt-Lead Alloys.

the mixture to  $1400^\circ$  in magnesia crucibles in an atm. of hydrogen. The products with 22.8 to 95.1 per cent. of cobalt behaved as mixtures, and no evidence of the formation of definite chemical compounds was observed. K. Lewkonja obtained the f.p. curves indicated in Fig. 40. The two elements are partially miscible in the liquid state. Molten alloys with over 3 per cent. or more than 99 per cent. of cobalt cannot be obtained. In the solid state, neither compounds nor solid soln. are formed. W. Oelsen found that lead dissolved  $11 \times 10^{-4}$  to  $21 \times 10^{-4}$  per cent. of cobalt. W. Seith and A. Keil, and K. Fischbeck discussed the diffusion of cobalt in lead; and W. Guertler and H. Schack, alloys with sulphur.

E. Haynes,<sup>10</sup> and F. Wever and U. Haschimoto prepared **chromium-cobalt alloys**; H. C. Peffer and H. C. Pierce obtained the alloys electrolytically; and K. Lewkonja studied the f.p. curves. Cobalt and chromium are miscible in all proportions in the liquid and solid states. The minimum temp. at which crystallization commences is  $1320^\circ$  when the fused mass has 47 per cent. of chromium. Alloys with 30 to 100 per cent. of chromium undergo a change in structure at about  $1226^\circ$ , for the crystals of the homogeneous solid soln. primarily formed in the cooling process are transformed into two different kinds of crystals, which are readily distinguished when a polished surface of the metal is etched by electrolysis. The modifications of F. Wever and co-workers, and R. Ruer and co-workers are summarized in Fig. 41; the subject was discussed by A. Michel and P. Benazet,

and J. A. M. van Liempt. F. Wever and U. Haschimoto found the crystals of **cobalt monochromide**,  $\text{CoCr}$ , to be probably tetragonal, with 8 mols. in the elementary cell, and the parameters  $a=5.33 \text{ \AA.}$ , and  $c=7.20 \text{ \AA.}$  The equilibrium conditions of this compound and of **cobalt hemichromide**,  $\text{Co}_2\text{Cr}_3$ , are indicated in Fig. 41. F. Wever and U. Haschimoto used ammonium persulphate as an etching soln. for the alloys. The hardness attains a maximum with about 70 per cent. of chromium; the tensile strength rises to 90 kgrms. per sq. mm. with 30 per cent. of chromium. The mechanical properties were also studied by E. Haynes, H. T. Kalmus, and G. Tammann. W. H. Souder and P. Hindert gave for the mean coeff. of linear expansion of an alloy with 20 per cent. of chromium, 0.04141 between  $20^\circ$  and  $100^\circ$ ; 0.04052 between  $20^\circ$  and  $300^\circ$ ; and 0.04161 between  $20^\circ$  and  $600^\circ$ . A. W. Smith studied the thermal conductivity. Observations on the magnetic properties were made by K. Honda, F. Wever and co-workers, and R. Ruer and co-workers. K. Lewkonja found that at room temp., alloys with up to 25 per cent. of chromium are magnetizable, and alloys with 15 per cent. of chromium possess the greatest magnetic intensity:

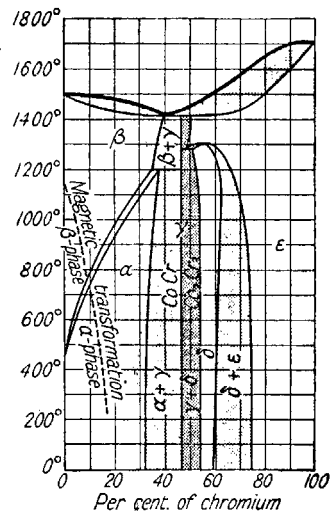


FIG. 41.—The Freezing-point Curves of Chromium-Cobalt Alloys.

Chromium . . . . .	0	10	15	20	25 per cent.
Magnetic intensity . .	15.70	22.50	33.80	5.28	0.20 (relative)
Loss of magnetism . .	1056°	686°	300°	—	—

E. Haynes found that alloys with 10 to 60 per cent. of chromium, and free from sulphur, remain bright in the atm. of a laboratory, and an alloy with 25 per cent. of chromium at about  $500^\circ$  became straw-yellow, and at a higher temp., bronze-yellow, purple, blue, and bluish-black. G. Tammann and W. Köster observed that alloys with 20 to 40 per cent. of chromium, when heated between  $500^\circ$  and  $800^\circ$  for 1 hr., acquire a film of oxide at a rate in accord with an exponential law. F. Wever and U. Haschimoto found that the velocity of oxidation at  $700^\circ$  to  $1000^\circ$  decreases with increasing proportions of chromium; at  $1100^\circ$  to  $1200^\circ$ , an alloy with 30 per cent. of chromium holds the oxide film tenaciously, and is less attacked than alloys with 20 to 40 per cent. of chromium which in turn readily give a scaling oxide. W. Guertler and T. Liepus observed that the 1:1-cobalt-chromium alloy was attacked within 8 hrs. by 10 and 50 per cent. nitric acid; 10 and 36 per cent. hydrochloric acid; aqua regia; 10 per cent. sulphuric acid, and 20 per cent. sulphuric acid sat. with sodium sulphate; carbon dioxide and air; acetic, citric, and tartaric acids; and 10, 50, and 70 per cent. aq. ammonia. A 10 per cent. soln. of sodium hydroxide did not attack the alloy in 48 hrs., but a 50 per cent. soln. did so in 8 hrs., and a soln. with hydrogen dioxide did not attack the alloy in 48 hrs. A 10 per cent. soln. of sodium sulphide did not attack the alloy in 48 hrs., but a 50 per cent. soln. did so in 8 hrs., and a soln. with 4 per cent. of sodium sulphide and 8 per cent. of alkali did so in 8 hrs. Chlorine water did not attack the alloy in 8 hrs., whilst sea-water, sea-water and air, rain-water and air, and a soln. of magnesium chloride did not do so in 48 hrs. A 1:500-soln. of mercuric chloride is decomposed by the alloy. W. Rohn found that with un-annealed and annealed samples of a Co:Cr (90:10)-alloy, the loss in grams per sq. dm. with 10 per cent. nitric acid was respectively 12.9 and 9.5 in 24 hrs. cold, and 15 and 17.3 in 1 hr. hot; 10 per cent. sulphuric acid, respectively 0.027 and 0.012 in 24 hrs. cold, and 2.7 and 2.4 in 1 hr. hot; and 10 per cent. hydrochloric

acid, respectively 0.13 and 0.06 in 24 hrs. cold, and 1.5 and 1.2 in 1 hr. hot. G. Masing studied the age-hardening of **copper-silicon-chromium-cobalt alloys**. W. Köster studied the **chromium-cobalt-iron alloys**.

C. L. Sargent<sup>11</sup> prepared **cobalt-molybdenum alloys** by heating mixtures of the oxides of these metals with sugar charcoal in an electric furnace; and U. Raydt

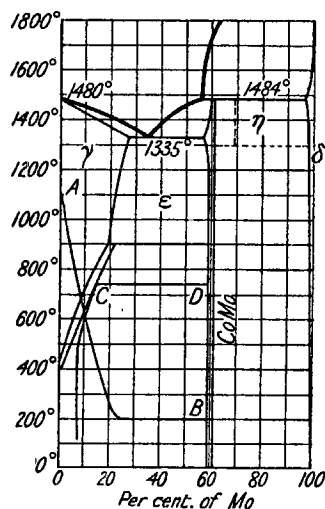


Fig. 42.—Freezing-point Curves of Cobalt-Molybdenum Alloys.

forms rounded crystallites. The curve *AB* represents the magnetic transformation of the  $\gamma$ -solid soln.; and *CD*, of the  $\epsilon$ -solid soln. T. Takei added the dotted lines to Fig. 42, to accord with his examination of the X-radiograms. These indicate the existence of alloys rich in cobalt,  $\gamma$ , with a face-centred, cubic lattice; alloys rich in cobalt, with a hexagonal lattice, with indications of the molybdiide,  $\text{CoMo}$ ,  $\epsilon$ , of **cobalt hemitrimolybdiide**,  $\text{Co}_2\text{Mo}_3$ ,  $\eta$ , and of the solid soln.,  $\delta$ , containing 2 per cent. of cobalt. R. Vogel observed that the solid soln. with 20 per cent. molybdenum exhibit deformation twinning. V. Adelsköld and co-workers studied the system  $\text{Co-Mo-C}$ , but observed no formation of a complex carbide. W. Köster and W. Tonn studied the magnetic properties of the alloys.

F. Wever and U. Haschimoto observed the action of dil. nitric acid, and of citric acid; and E. Haynes, the action of nitric, hydrochloric, and sulphuric acid. E. Haynes found that alkali-lye does not attack the 25 per cent. alloy during 1 hour's boiling; F. Wever and U. Haschimoto, and W. Borchers examined the influence of additions of copper, aluminium, silicon, molybdenum, tungsten, manganese, iron, and nickel on the acid-resistance of the alloys. W. Guertler and T. Liepus found that a 70:30-alloy of cobalt and molybdenum was attacked in 8 hrs. by a 10 per cent. soln. of sulphuric acid, and by 20 per cent. sulphuric acid sat. with sodium sulphate; by carbon dioxide and air; acetic acid; citric acid; tartaric acid; by 10 and 50 per cent. soln. of sodium hydroxide; 10 and 50 per cent. aq. ammonia; 10 per cent. sodium sulphide; chlorine water; sea-water; sea-water plus air; rain-water plus air; and a soln. of magnesium chloride. No attack was observed after 24 hrs. in contact with 10 and 50 per cent. nitric acid; 10 and 35 per cent. hydrochloric acid, or with aqua regia. No action was observed after 8 hrs' contact with soda-lye and hydrogen dioxide, or with a mixture of 4 per cent. sodium sulphide and 8 per cent. alkali. K. Kreitz studied the action of nitric acid.

C. L. Sargent studied the alloys with carbon. L. F. Dreiholz studied the ternary system; **copper-molybdenum-cobalt alloys**; and W. Guertler made

some observations on the technical applications of these alloys. W. Guertler and T. Liepus studied the action of various reagents on a copper-molybdenum-cobalt alloy. H. Schirmeister prepared a few **aluminium-molybdenum-cobalt alloys**, and found that they behaved like those with tungsten in place of molybdenum (*q.v.*). E. Haynes also investigated some **chromium-molybdenum-cobalt alloys**. F. Stäblein studied their magnetic properties; and W. Guertler and T. Liepus examined the effect of various reagents on these alloys.

In 1860, F. A. Bernoulli<sup>12</sup> said that **cobalt-tungsten alloys** can be prepared only by the simultaneous reduction of the two metals. H. List said that the metals do not form true alloys. Alloys were also made by N. Drebes by reducing a mixture of tungsten and cobalt oxides with aluminium. A. Stavenhagen and E. Schuchard also obtained the alloys by the thermite process. C. L. Sargent, D. Kremer, F. Stein, K. Kreitz, and W. Geiss and J. A. M. van Liempt prepared the alloys by heating mixtures of the oxides with sugar charcoal in an electric furnace.

C. Agte and co-workers found that the solubility of cobalt in tungsten is near 10 at. per cent.; and of tungsten in cobalt, 8 at. per cent. Alloys with between 52 and 63 at. per cent. have an intermediate crystalline phase which on the tungsten side is non-magnetic, and they become magnetic as the proportion of cobalt increases. K. Kreitz's, W. P. Sykes', and W. Köster and W. Tonn's observations on the f.p. of the alloys are summarized in Fig. 43. There is evidence of the formation of two compounds: one is thought to be **cobalt hexitartstide**,  $\text{Co}_6\text{W}$ , melting at about  $1500^\circ$ ; and the other **cobalt tungstide**,  $\text{CoW}$ , melting at about  $1634^\circ$ . Alloys with 0 to 40 per cent. of tungsten consist of a series of solid soln.; and those with 40 to 70 per cent., of a mixture of the eutectic and solid soln.; or of eutectic and the monotungstide, according as the alloy contains less or more than 45 per cent. of tungsten. The eutectic is at  $1400^\circ$  and 44.5 per cent. of tungsten. *AB* represents the curve of magnetic transformation of the  $\gamma$ -solid soln.; and *CD*, of the  $\alpha$ -solid soln. C. Agte and co-workers also studied the system; and V. Adelsköld and co-workers observed that in the presence of carbon, the complex **cobalt tungsten tritacarbide**,  $\text{Co}_3\text{W}_3\text{C}$ , is formed. C. L. Sargent found the sp. gr. of alloys with 48.26, and 70.10 per cent. of cobalt to be respectively 10.96, and 8.92. According to K. Kreitz, the addition of tungsten to cobalt rapidly increases the brittleness, and Brinell's hardness of the alloys, thus:

Tungsten . . . . .	0	0.95	2.15	3.02	4.64	9.7	24.15 per cent.
Hardness . . . . .	185	188	196	202	214	282	288

N. Drebes found that the alloys with 75 to 95 per cent. tungsten are very hard. By annealing over  $1200^\circ$ , K. Kreitz found it possible to roll the alloys into thin plates. The sp. electrical resistance and conductivity respectively in ohms or mhos per cm. cube, for alloys carrying about 0.6 per cent. of iron, are:

Tungsten . . . . .	0	0.95	2.15	3.02	4.64	9.7	12.1	24.15 per cent.
Ohms $\times 10^4$ . . . . .	0.0980	0.0375	0.1905	0.2270	0.3130	0.4450	0.8060	0.7145
Mhos $\times 10^{-4}$ . . . . .	11.03	7.27	5.25	4.30	5.32	2.25	1.98	1.40

W. Geiss and J. A. M. van Liempt found that the concentration-temp. coeff. curve, Fig. 44, between  $-183^\circ$  and  $20^\circ$  shows nothing of the existence of a continuous series of solid soln. There are probably two or more kinds of solid soln., and also,

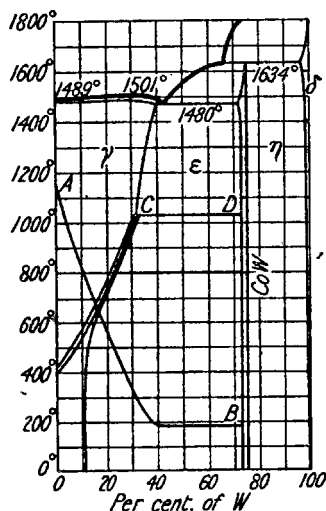


FIG. 43.—Freezing-point Curves of the Cobalt-Tungsten Alloys.



possibly compounds. W. Köster and W. Tonn studied the magnetic properties of the alloys; and C. Agte and co-workers found that the relative magnetization,  $I$ , of the alloys increases as the atomic percentage of cobalt increases:

Co . . .	0	55	57	65	72	90	95	100
$I$ . . .	0	0	0.47	2.8	10.2	44.0	61.1	100

F. Stein found that alloys with up to 3 per cent. of tungsten are more readily attacked by sulphuric acid than is cobalt, but with increasing proportions of tungsten, the resistance is greater. Thus, representing the corrosion in mgrms. per sq. mm. per hour:

Tungsten . . .	0	0.95	2.15	3.025	4.64	5.02	9.75	12.01 per cent.
Corrosion {	20° . . .	0.0.65	0.0.25	0.0.72	0.00135	0.0012	—	0.0.61 0.0.3
	98° . . .	0.0154	0.0176	0.84	1.203	1.055	1.09	0.29 0.098

The solubility in mgrms. per sq. mm. per hour in a soln. of 2 per cent. sodium chloride mixed with 5 per cent. nitric acid at 98°, is for alloys with 0, 3.025, 5.02, and 12.01 per cent. of tungsten, respectively 0.0482, 0.334, 0.406, and 0.736.

J. L. Gregg and C. W. Küttner, L. L. Wyman and F. C. Kelley, S. L. Hoyt, and K. Schröter studied the alloys with carbon. H. Schirmeister found that in the **aluminium-tungsten-cobalt alloys**, the addition of a small proportion of tungsten raised the tensile strength of the aluminium-cobalt alloys, and made the fracture finer. Larger proportions of tungsten were injurious. The best proportions were 0.8 to 1.2 per cent. of tungsten. The hardness is proportional to the amount of cobalt in the alloy. The alloys are

easy to work, take a good polish, and resist the action of the air. The sp. gr. is 2.8 to 2.9.

E. Haynes prepared some **chromium-tungsten-cobalt alloys**. O. Rumschöttel found that tungsten separated out in the freezing of alloys made by adding an alloy

of cobalt and tungsten to one of zinc and copper. Alloys were also made by L. Guillet and H. Godfroid, A. Hofmann, G. L. Kronfeld, E. Schiffer, and E. H. Schulz and co-workers. W. Oertel and E. Pakulla studied the f.p. of the alloys. The structure of the alloys was studied by C. W. Drescher, T. Spooner, H. Brösamlen, W. H. Losee, S. B. Wright, H. J. French and H. K. Herschmann, L. Guillet and H. Godfroid, A. V. Harris, A. Hofmann, K. Löbbecke, W. Oertel and E. Pakulla, and E. H. Schulz and co-workers. W. Köster's observations on the nature of the solid soln. are summarized in Fig. 45. C. W. Drury found that a stellite with a low proportion of tungsten had a face-centred, cubic lattice with

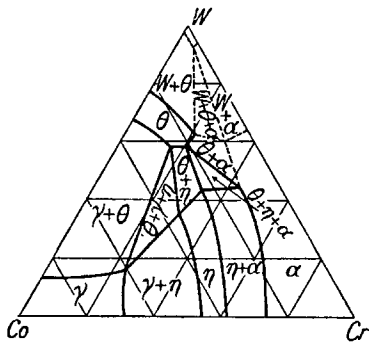


FIG. 45.—Phases in the Ternary System: Co—Cr—W.

$a=3.554$  to  $3.585$  A. W. Oertel and E. Pakulla studied the mechanical properties of these alloys, and of alloys with molybdenum in place of tungsten. E. Haynes' alloy, called *stellite*, is usually composed of chromium, cobalt, and tungsten, and it may be modified by the addition of iron, or by the substitution of some molybdenum for tungsten, or nickel for cobalt—e.g., (i) soft malleable stellite has Co, 80; Cr, 20 per cent.; (ii) hard, malleable stellite has Co, 55; Cr, 40; W, 3; and C, 2 per cent.; and another stellite (iii) has Co, 55; Cr, 35; and W, 10 per cent. Other alloys of a similar character have the trade-names *celsite*, *cædite*, *volomit*, *thoran*, *akrit*, *widia*, etc. K. Löbbecke said that the average composition of the stellite alloys is Co, 55;

Cr, 28; W, 15; C, 2.5 with small proportions of impurities, chiefly iron. The hardness increases with increasing chromium and decreasing cobalt-content, but tungsten has very little influence on the hardness. An increase in the proportion of carbon causes at first an increase in hardness followed by a fall to a constant value owing to the formation of graphite. The resistance to wear increases generally with decreasing cobalt-content; the chromium and tungsten have very little influence. The subject was studied by G. S. Armstrong, F. Bauerfeld, C. W. Drury, L. Guillet, E. Guillet and H. Godfroid, W. H. Losee, M. Märkle, S. Malowan, A. Merz and W. Schütz, W. Oertel and E. Pakulla, F. Rapatz, E. H. Schulz and co-workers, and R. Walter. W. H. Souder and P. Hidnert found for the coeff. of thermal expansion,  $\alpha$ , of the three samples of stellite just indicated:

	20°-100°	100°-200°	200°-300°	300°-400°	400°-500°	500°-600°	20°-600°
$\alpha \times 10^6$ { i	14.1	15.1	16.2	15.9	16.0	18.9	16.1
ii	13.4	15.2	16.0	16.3	17.5	20.2	16.5
iii	11.0	12.3	13.6	13.8	13.3	16.9	13.6

E. H. Schulz and W. Jenge observed that the alloy melts near 1250°. W. W. Coblenz found the reflecting power,  $R$ , for wave-lengths  $\lambda$  in  $\mu=0.001$  mm., to be:

$\lambda$	0.45	0.50	0.70	0.90	1.00	1.50	2.00	3.00	4.00 $\mu$
$R$	63.5	65.8	71.8	73.5	74.0	75.3	76.8	80.0	82.8 per cent.

I. C. Gardner, E. O. Hulburt, P. R. Gleason, W. W. Coblenz and co-workers, and G. G. Abbot and co-workers, also measured the reflecting power of stellite. E. Haynes, and W. Oertel and E. Pakulla observed that a blue, protective film was formed when the alloy was exposed to 1000°. The alloy is attacked by hydrofluoric, hydrochloric, and sulphuric acids and by molten alkalis; but it is scarcely affected by phosphoric, and organic acids, alkali-lye, and by soln. of ammonium and mercuric chlorides. E. Schiffer said that the powdered alloy dissolves slowly in aqua regia, bromine aqua regia, bromine and hydrochloric acid, and in a soln. of potassium chlorate in a mixture of hydrochloric and sulphuric acids. E. Deiss studied the action of hydrochloric acid, and molten sodium dioxide and carbonate. W. Oertel and E. Pakulla examined the action of aqua regia, hydrochloric, sulphuric, nitric, oxalic, and tannic acids, sea-water, potash-lye, and a sulphuric acid soln. of copper sulphate. E. Cremer and B. Fetkenheuer observed that the alloys are attacked by molten potassium hydrosulphate, or by a mixture of sodium carbonate and potassium carbonate and nitrate. J. G. Thompson and co-workers studied the action of soln. of urea and of ammonium carbamate. K. Löbbecke studied the corrodibility of the alloys in hydrochloric acid, and E. H. Schulz and W. Jenge found that the alloy begins to oxidize in air at about 1000°; and it is stable in contact with hydrofluoric and sulphurous acids, and a soln. of mercuric chloride. K. Löbbecke observed that the alloy most resistant to corrosion by hydrochloric or acetic acid is the Co:Cr:W:C=55:28:15:2.5 alloy indicated above. The resistance to corrosion is sensitive to the proportion of contained carbon. Observations on a similar alloy, *akrit*, with cobalt 38 per cent.; Cr, 30; W, 16; Ni, 10; Mo, 4; and C, 2 to 5, were made by E. H. Schulz, and C. W. Drescher. W. Oertel and E. Pakulla studied the **molybdenum-chromium-cobalt alloys**. A. Stavenhagen and E. Schuchard prepared **tungsten-molybdenum-chromium-cobalt alloys**, as well as **uranium-cobalt alloys**, by the thermite process. P. A. Heller obtained uranium-nickel alloys by fusing uranium carbide and nickel oxide in a carbon crucible in an arc furnace. The alloys contained 4.5 to 5 per cent. of carbon.

K. Hiege<sup>13</sup> prepared **cobalt-manganese alloys**, and found that they form a continuous series of solid soln. with a flat minimum at about 30 per cent. of cobalt and 1150°, Fig. 46. The crystals are not homogeneous but become nearly so after the alloys have been annealed for 5 hrs. in magnesia at 1000°. The magnetic transformation curve falls rapidly from 1150° with increasing proportions of manganese. G. Tammann and E. Vaders studied the e.m.f. of the alloy, and

observed that the limit of the solid soln. has about 0.50 mol. Co. The subject was studied by J. A. M. van Liempt. E. Persson and E. Oehlman made observations

on the X-radiograms—*vide* manganese; B. Blumenthal and co-workers, on the structure of the alloys; and W. Köster and W. Schmidt, the relation between the lattice structure and ferromagnetism.

G. Tammann and E. Vaders observed that with hydrochloric acid, alloys with less than 39.6 per cent. of manganese develop no hydrogen, but with higher proportions, hydrogen is developed. G. Arrivaut found that soln. of ammonium chloride, or hydrofluoric, hydrochloric, sulphuric, or nitric acid dissolve alloys with 60 to 85 per cent. of manganese completely. Alcoholic soln. of acetic acid and ammonium acetate dissolve most of the man-

ganese, leaving a pyrophoric residue with about 5 per cent. of manganese. W. Guertler and T. Liepus found that the 1:1-cobalt-manganese alloy was attacked in 8 hrs. by 10 and 50 per cent. nitric acid; by 10 and 36 per cent. hydrochloric acid; aqua regia; 10 per cent. sulphuric acid, and 20 per cent. sulphuric acid sat. with sodium sulphate; carbon dioxide and air; acetic acid; tartaric acid; citric acid; 10 and 50 per cent. sodium hydroxide; sodium hydroxide and hydrogen dioxide; 10, 50, and 70 per cent. aq. ammonia; 10 and 50 per cent. sodium sulphide, and 4 per cent. sodium sulphide mixed with 8 per cent. alkali; chlorine water; sea-water; sea-water plus air; rain-water plus air; and magnesium chloride soln. It decomposed a 1:500-soln. of mercuric chloride. The action on the alloy Co: Mn: Mo=40:50:10 by nitric acid, hydrochloric acid, aqua regia, citric acid and tartaric acid; soda-lye; sodium sulphide; sea-water; and magnesium chloride soln. was studied. W. Guertler and T. Liepus also examined **cobalt-manganese-molybdenum alloys**.

According to A. F. Gehlen,<sup>14</sup> J. F. Hassenfratz, T. Fleitmann, P. Oberhoffer, C. J. B. Karsten, J. Percy, F. Toldt, J. Stodart and M. Faraday, J. L. F. Vogel, R. A. Hadfield, W. Pruszkowsky, and G. H. Billings, the **iron-cobalt alloys** can be readily formed. The alloy is malleable and weldable; it is not cold-short, but inclined to be red-short. R. A. Hadfield noted that cobalt raises the elasticity of iron. P. Berthier observed that the alloys of iron with cobalt closely resemble those with nickel. O. E. Erdmann, and A. Weiske observed that traces of cobalt occur in many commercial irons. C. F. Burgess and J. Aston found that alloys with up to 6 per cent. of cobalt can be forged without difficulty at the normal forging temp.; alloys with less than 6 per cent. of cobalt can be welded electrically; and all can be machined in the lathe. The electrolytic production of the alloys was discussed by G. Bruni and M. Amadori, H. J. Blikslager, S. Glasstone and J. C. Speakman, and H. W. Töppfer; and the electrometallurgy of the alloys, by F. Peters. The diffusion of cobalt in iron was studied by J. Laissus, and N. Ageeff and M. Zamotorin. A selection from W. van Drunen's results for the diffusion coeff., *D*, are as follow:

TABLE III.—THE DIFFUSION OF COBALT INTO IRON.

1250° (72 hrs.)			1300° (72 hrs.)			1350° (48 hrs.)			1400° (48 hrs.)		
Depth cm.	Cobalt %	<i>D</i> × 10 <sup>8</sup>	Depth cm.	Cobalt %	<i>D</i> × 10 <sup>8</sup>	Depth cm.	Cobalt %	<i>D</i> × 10 <sup>8</sup>	Depth cm.	Cobalt %	<i>D</i> × 10 <sup>8</sup>
0.00225	34.8	0.553	0.00250	41.5	0.146	0.00250	44.6	0.846	0.00125	45.7	0.334
0.00725	16.0	0.887	0.01360	13.0	0.229	0.01300	16.6	0.448	0.01050	25.1	0.480
0.01225	3.1	0.718	0.02450	0.8	0.169	0.01850	6.2	0.361	0.02250	4.1	0.418

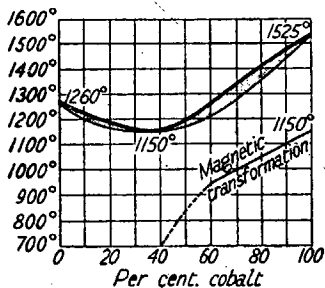
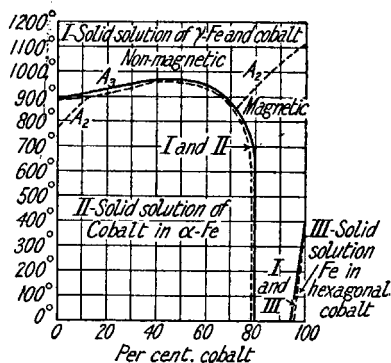
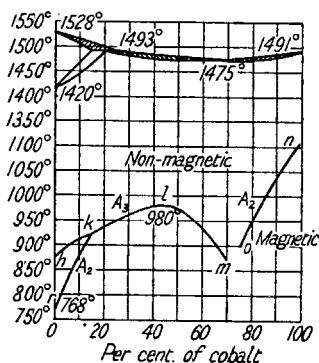


FIG. 46. — The Freezing-point Curves of the Manganese-Cobalt Alloys.

The equilibrium diagram has been worked out by W. Guertler and G. Tammann. They found for the f.p. of mixtures on the heating and cooling curves :

Cobalt	.	0	5	13	30	50	60	80	100 per cent.
Heating	.	1485°	1440°	1430°	1435°	1435°	1425°	1430°	1435°
Cooling	.	1475°	1440°	1440°	1445°	1440°	1445°	1440°	1450°

Cobalt has very little influence on the m.p. of iron. Fig. 47 is due to R. Ruer and K. Kaneko. Iron has a transformation point at 1420° when  $\delta$ -iron becomes  $\gamma$ -iron. This temp. is raised by the addition of cobalt. The f.p. curve has two branches one of which has a minimum at 1475° and 65 per cent. of cobalt. The two branches, which correspond with the f.p. of two series at solid soln., intersect at 1493° and 15·5 per cent. of cobalt. The thermal changes at lower temp. agree with the magnetic changes. The  $\gamma \rightarrow \beta$ , and the  $\beta \rightarrow \alpha$  transformations coincide from 15 per cent. of cobalt onwards, and they increase with increasing cobalt. The transformation curve passes through a maximum at 980° and 45 per cent. of cobalt; and the eutectoidal point must lie somewhere between 70 and 75 per cent. of cobalt. The curve *hkl*, Fig. 47, represents the reversible transformation of the  $\alpha$ -phase to the  $\gamma$ -phase; *rk*, the reversible magnetic transformation of the  $\alpha$ -phase; and *on*, the curve of reversible transformation of the non-magnetic  $\beta$ -cobalt to the magnetic  $\alpha$ -cobalt. The diagram was discussed by A. Kußmann and co-workers, J. A. M. van



Figs. 47 and 48.—Equilibrium Diagram of the Cobalt-Iron Alloys.

Liempt, L. Grenet, and F. Wever. P. Weiss said that the magnetic transformation agrees with the existence of **cobalt diferride**,  $\text{Fe}_2\text{Co}$ . W. Guertler and G. Tammann said that the alloys rich in cobalt, i.e. those with 75 to 100 per cent. of cobalt, suffer the magnetic transformation at the same temp.; alloys with 60 to 75 per cent. of cobalt suffer a more gradual transformation, for there is an interval of about 100° between the heating and cooling curves; alloys with 5 to 60 per cent. cobalt show an undercooling effect of 20° to 30°; and the alloys rich in iron—i.e. with less than 5 per cent. cobalt—suffer transformation like iron at about 760°. With repeated heatings, the temp. at which magnetization vanishes, increases up to 820°; while the temp. at which magnetization returns, is about constant at 752°. H. Scott found that cobalt did not have a marked effect on the conversion of martensite to troostite. H. Masumoto's results for the equilibrium of the solid alloy are shown in Fig. 48. There is a transformation point for cobalt at 403°, and this corresponds with a region where the solid soln. of the  $\gamma$ -iron and cobalt forms a solid soln. of  $\gamma$ -iron in hexagonal cobalt. Both the  $A_4$ - and  $A_3$ -arrests are raised by the addition of cobalt. The effect of cobalt in the  $A_2$ - and  $A_3$ -arrests was found to be :

Fe	.	21·14	27·13	40·11	55·08	65·06	80·04	100 per cent.
Ac <sub>2</sub>	.	943°	908°	—	—	—	—	—
Ar <sub>2</sub>	.	932°	875°	—	—	—	—	—
Ac <sub>3</sub>	.	874°	863°	938°	981°	955°	920°	908°
Ar <sub>3</sub>	.	407°	833°	930°	970°	964°	927°	888°

A. Osawa found that in the case of the  $\alpha$ -solid soln. of iron and cobalt the lattice-constant concentration curve is of the second degree.

Iron . . .	95	90	80	60	50	25	24 per cent.
<i>a</i> . . .	2.855	2.854	2.851	2.847	2.846	2.825	2.825 A.
Iron . . .	20	10	5	3	1.5	1.0	0.5 per cent.
<i>a</i> . . .	2.824	—	—	—	2.493	2.493	2.492 A.
<i>c</i> . . .	3.434	3.541	3.536	3.533	4.066	4.062	4.062 A.

The cobalt-carbon system, studied by G. Boecker, A. Schulze, W. C. Ellis, E. L. Reed, R. Vogel and W. Sundermann, L. Grenet, and by O. Ruff and F. Keilig, has been discussed in connection with the carbides—5. 39, 20. At 1700°, cobalt dissolves 3.9 per cent., and at the eutectic temp., 1300°, cobalt retains 0.82 per

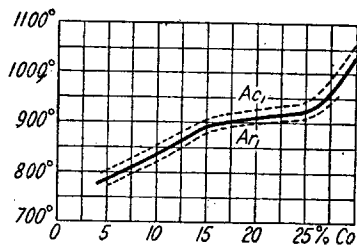


FIG. 49.—The Effect of Cobalt on the  $A_1$ -arrest of 0.2 per cent. Carbon Steel.

cent. of carbon in solid soln. The presence of a carbide in the eutectic cannot be proved; for the eutectic appears to contain only graphite and crystals of cobalt. J. O. Arnold and A. A. Read thought that they could demonstrate the existence of a cobalt cementite,  $\text{CoC}_3$ , by the method of residual analysis. The negative heat of formation of this carbide, as determined by O. Ruff and co-workers, is not so great as to exclude the possibility of its existence in cobalt steels. J. O. Arnold and A. A. Read observed that cobalt has a smaller tendency than nickel to produce graphite; and

O. Bauer and E. Piwowarsky observed with respect to cast iron that up to 2 per cent. of cobalt serves no useful purpose, but it has a tendency to retain carbon in the combined state. L. Guillet observed that steels with up to 40 per cent. of cobalt are all pearlitic even when they contain 0.80 per cent. of carbon. L. Dumas represented the effect of cobalt on the  $A_1$ -transformation of a steel with 0.2 per cent. of carbon by Fig. 49. J. O. Arnold said that cobalt does not form a "true" steel having 100 per cent. pearlite. H. Sawamura, and F. Roll showed that cobalt favours the decomposition of the carbide in cast iron; Y. Umansky and E. Gordon, the lattice structure of the contained martensite; A. Michel and P. Bénazet, and E. Prêtet studied the effect of cobalt on the tempering of the quenched alloy; and L. Grenet, the transformation of the alloys from one state to another.

According to M. R. Andrews, and Z. Nishiyama, the iron-cobalt alloys have a body-centred cubic lattice with up to about 70 at. per cent. of cobalt; and the effect of adding cobalt to iron is to reduce the grating space from  $a=2.850$  A. for iron, to  $a=2.827$  A. for an alloy with 66.7 per cent. of cobalt. The change is not linear. Alloys with 90 to 98 per cent. of cobalt are face-centred cubic with  $a$  from 3.550 A. to 3.540 A., and alloys with about 70 to 80 per cent. of cobalt have mixed lattices. Cobalt alone at room temp. has a close-packed, hexagonal space-lattice. Z. Nishiyama found the lattice constant,  $a$ , of alloys with 5, 10, 15, and 20 per cent. of cobalt,  $a=2.867$  A., 2.867 A., 2.867 A., and 2.868 A. respectively. H. Perlitz discussed the distance apart of the atoms. Z. Nishiyama found for the sp. gr., at 13.4° to 13.8°, of alloys with 5, 10, 15, and 20 per cent. of cobalt, the respective values 7.8811, 7.9002, 7.9133, and 7.9411; W. Brown found that the sp. gr. and sp. vol. of steels with 0.25 per cent. carbon and 1.8 per cent. cobalt, were respectively 7.8117 and 0.12801, and with 0.52 per cent. carbon and 7.0 per cent. nickel, respectively 7.8326 and 0.12767. Hence, with up to 7 per cent. of cobalt, the sp. vol. decreases at the rate of 0.0001 c.c. for every per cent. of added cobalt. A. Osawa, A. Preuss, P. Dejean, and B. Simmersbach discussed this subject. L. Guillet found the following mechanical properties for cobalt steel with about 0.8 per cent. of carbon:

Cobalt . . . . .	4.45	6.72	9.76	29.30 per cent.
Elastic limit . . . . .	46.6	51.1	44.0	50.5 kgrms. per sq. mm.
Tensile strength . . . . .	121.8	102.3	122.6	118.5 " " "
Elongation . . . . .	6	7	5	6 per cent.
Reduction of area . . . . .	10.6	14.6	6.8	11.5 " " "
Brinell's hardness . . . . .	248	241	248	241 " " "

L. Guillet added that the presence of cobalt slowly raises the tensile strength and elastic limit while diminishing the elongation and reduction of area. There is no sudden alteration in the mechanical properties, which are changed only gradually. Observations were also made by C. E. Guillaume, K. Honda, E. K. Smith and H. C. Aufderhaar, L. Guillet, K. Sasagawa, R. Scherer, I. Musatti and G. Calbiani, J. Stodart and M. Faraday, R. A. Hadfield, K. Taniguchi, and C. B. Browne. G. Tammann and V. Caglioti studied the recovery of the hardness after cold-working. L. Dumas' results with steel containing 0.2 per cent. of carbon are summarized in Fig. 50. The observations of J. O. Arnold and A. A. Read are as follows :

Carbon (combined) . . . . .	0.64	0.62	0.84	0.93	0.72 per cent.
Cobalt . . . . .	2.68	5.50	11.18	16.97	20.85 " "
Yield-point . . . . .	45.3	51.1	50.5	58.8	62.0 kgrms. per sq. mm.
Tensile strength . . . . .	75.0	75.8	108.8	116.8	110.5 " " "
Elongation . . . . .	17.5	22.5	11.5	9.5	11.0 per cent.
Reduction of area . . . . .	26.7	42.7	21.5	12.7	18.9 " " "
Number imparts for fracture . . . . .	242	233	158	174	123

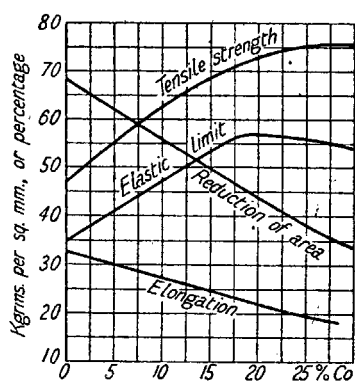


FIG. 50.—The Mechanical Properties of 0.2 per cent. Carbon Steel.

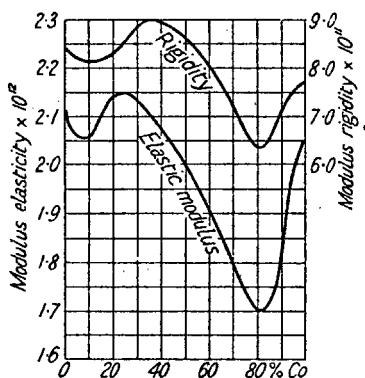


FIG. 51.—Modulus of Elasticity and Rigidity of Iron-Cobalt Alloys.

H. T. Kalmus and K. B. Blake said that the  $\text{Fe}_2\text{Co}$ -alloy can be readily forged, and it then has twice the strength of purified iron; mechanically the alloy is brittle, but when annealed, it has the same ultimate strength as purified iron. T. D. Yensen gave for purified iron, and the  $\text{Fe}_2\text{Co}$ -alloy, both melted in vacuo, as forged, gave the respective values 40,600 and 73,400 lbs. per sq. in. for the stress at the yield-point; 42,630 and 97,500 lbs. per sq. in. for the ultimate strength; 32 and 3 per cent. for the elongation; and 71.0 and 3.0 per cent. for the reduction of area. For the same samples annealed, he gave the respective values 16,100 and 30,800 lbs. per sq. in. for the yield-point; 35,500 and 30,800 lbs. per sq. in. for the ultimate stress; 49.0 and 1.0 per cent. for the elongation, and 78.0 and 1.0 per cent. for the reduction of area. K. Honda gave for the Young's modulus of elasticity,  $E$ , and the rigidity, or torsion modulus,  $n$  :

Co . . . . .	0	10	20	30	40	70	80	90	100 per cent.
$E \times 10^{-12}$ . . . . .	2.087	2.030	2.119	2.132	2.068	1.836	1.703	1.934	2.038
$n \times 10^{-11}$ . . . . .	8.34	8.14	8.30	8.86	8.93	7.24	6.30	7.25	7.63

Thus, by adding cobalt to iron, Young's modulus decreases slightly, reaches a

minimum with 10 per cent. of cobalt, Fig. 51, then rises to a maximum with 27 per cent., and then gradually decreases to a second minimum at 82 per cent. Above this concentration, the modulus then rises to the value for cobalt alone. The change of the modulus of rigidity with concentration gives a similar graph with one maximum and two minima. The relative positions of the maxima and minima in the two curves nearly coincide each to each. Z. Nishiyama found the elastic moduli of alloys with 5, 10, 15, and 20 per cent. of cobalt, the respective values  $E \times 10^{-6} = 2.159, 2.171, 2.186, \text{ and } 2.238$  kgrms. per sq. cm. H. J. French and W. A. Tucker, W. Oertel and F. Pölguter, R. C. Good, A. L. Norbury, E. Kothny, A. R. Page and J. H. Partridge, P. Blum, O. J. Steinhart, and A. Schulze studied the physical properties of the alloys.

H. Masumoto and S. Nara found the coeff. of thermal expansion,  $\alpha$ , of the iron-cobalt alloys between 30° and 100° to be :

Cobalt	.	.	0	9.91	19.96	29.95	39.93 per cent.
$\alpha \times 10^6$	.	.	1.220	1.61	0.985	0.934	0.994
Cobalt	.	.	49.91	59.89	79.86	98.62	100 per cent.
$\alpha \times 10^6$	.	.	0.849	0.883	1.169	1.225	1.279

The results, plotted in Fig. 52, show that as iron is added to cobalt, the coeff. of thermal expansion decreases gradually to a minimum at about 47 per cent. of iron,

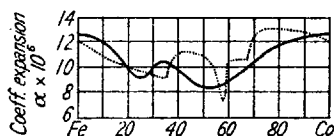


FIG. 52.—Coefficients of Thermal Expansion of the Iron-Cobalt Alloys.

it then increases to a maximum with 65 per cent. of iron; there is then a gradual decrease to a minimum at 73 per cent. of iron, and thereafter a steady increase to the value for iron alone. The break with 4 per cent. of iron approximates with the point at which the lattice-change occurs.

H. Masumoto and S. Nara's results are represented by the continuous line, Fig. 52, and those of A. Schulze, by the dotted line. H. Masumoto found breaks with 79 and 95 per cent. of cobalt and an inconspicuous maximum with 35 per cent. of cobalt. W. C. Ellis, and E. A. Blomqvist studied this subject. W. Brown found that the sp. hts. of the two steels just indicated were respectively 0.1153 and 0.1157. K. Honda and co-workers found the thermal conductivity,  $k$ , in c.g.s. units, to be :

Co	.	0	10	20	50	70	80	90	100 per cent.
$k$	.	0.1090	0.0944	0.1047	0.1700	0.1721	0.1223	0.0960	0.1653
$K \times 10^{-4}$	.	6.02	4.04	4.25	8.90	10.86	7.48	6.21	11.64
$k/K \times 10^6$	.	1.82	2.10	2.46	1.91	1.59	1.56	1.54	1.42

The results are plotted in Fig. 53, and they should be compared with the corresponding values for the nickel-iron alloys. The conductivity thus decreases at first with increasing proportions of cobalt; then attains a maximum with about 10 per cent. of cobalt, then rises to a maximum with about 65 per cent., and falls to a second minimum with about 90 per cent., after which it rises to the value for cobalt alone. K. Honda found an increase of about 1 microhm per cm. cube for the addition of 1 per cent. of cobalt to iron. K. Honda's values for the electrical conductivity,  $K \times 10^{-4}$  mho, are indicated above, and plotted in Fig. 53. The curves for the thermal and electrical conductivities are similar, and have corresponding maxima and minima. The ratio of the two conductivities is not constant, but varies from  $2.4 \times 10^{-6}$  to  $1.4 \times 10^{-6}$ . T. D. Yensen gave 10 microhms at 20° for the approximate electrical resistance of the  $\text{Fe}_2\text{Co}$ -alloy melted in vacuo and annealed at 900°. This is near the value for iron alone; for the alloy melted in vacuo and annealed at 1100°, the resistance is 10.10 microhms at 20°—for G. W. Elmen's observations, *vide infra*, the cobalt alloys. R. Gans, A. Schulze, and W. C. Ellis studied this subject; and G. Tammann and V. Caglioti, the recovery of the resistance after cold-working. P. W. Bridgman found that the effect of pressure on the sp. resistance,  $R$ , of the iron-cobalt alloys can be represented by

$\delta R/R_0 = a\rho + b\rho^2$ , where  $a$  and  $b$  are constants, and the temp. coeff.,  $\alpha$ , between  $0^\circ$  and  $100^\circ$ :

Iron	0	10	20	33.3	50 per cent.
$30^\circ \left\{ \begin{array}{l} a \times 10^6 \\ b \times 10^{11} \end{array} \right.$	-0.958 0.68	-0.401 0.69	4.32 14	-0.796 0.6	-0.473 2.65
$75^\circ \left\{ \begin{array}{l} a \times 10^6 \\ b \times 10^{11} \end{array} \right.$	-0.960 1.04	-0.305 0.81	6.29 8.0	-0.643 0	-0.467 1.63
$R(30^\circ) \times 10^6$	6.62	8.29	9.91	5.84	5.78
$\alpha \times 10^3$	6.04	5.34	5.63	4.46	4.25
Iron	66.7	80	90.9	100 per cent.	
$30^\circ \left\{ \begin{array}{l} a \times 10^6 \\ b \times 10^{11} \end{array} \right.$	1.153 3.10	1.408 0.73	-1.413 0.62	-2.427 1.14	
$75^\circ \left\{ \begin{array}{l} a \times 10^6 \\ b \times 10^{11} \end{array} \right.$	0.898 4.61	1.346 0.39	-1.360 0.49	-2.450 1.00	
$R(30^\circ) \times 10^6$	10.37	19.34	18.12	10.52	
$\alpha \times 10^3$	2.41	2.18	2.75	6.35	

The results are plotted in Fig. 54, and the breaks represent the change from the body-centred to the face-centred cubic structure as the proportion of cobalt rises beyond about 70 per cent.

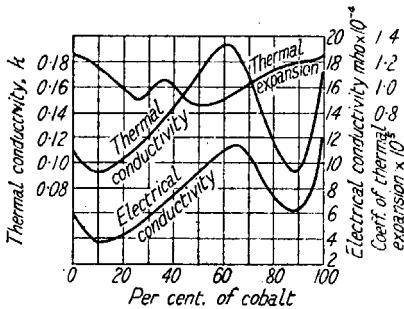


FIG. 53.—Electrical and Thermal Conductivities of the Cobalt-Iron Alloys.

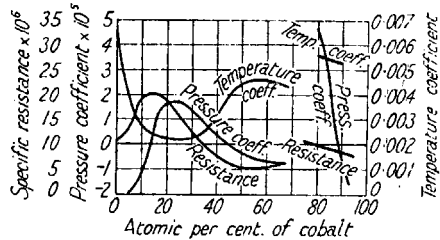


FIG. 54.—The Effect of Pressure on the Electrical Resistance of the Fe-Co Alloys.

T. S. Fuller found the thermoelectric force,  $E$  millivolts, of copper against iron alloys with 10, 20, and 30 per cent. of cobalt, between  $0^\circ$  and  $100^\circ$ , to be respectively  $-0.64$ ,  $-3.70$ , and  $-3.50$ . A. Schulze, and W. C. Ellis studied this subject.

K. Honda measured the intensity of magnetization,  $I$ , of a sequence of iron-cobalt alloys for fields of  $H$  gauss; the following results are selected from the tables:

5 per cent. Co	$\left\{ \begin{array}{l} H \\ I \end{array} \right.$	13.7 1117	113 1460	207 1551	689 1695	1179 1710
30 per cent. Co	$\left\{ \begin{array}{l} H \\ I \end{array} \right.$	25.3 1160	113 1643	207 1753	688 1844	1172 1868
90 per cent. Co	$\left\{ \begin{array}{l} H \\ I \end{array} \right.$	44.9 1067	146 1202	243 1260	720 1344	1160 1359

The intensity of magnetization,  $I$ , for an effective magnetizing field  $H=1200$  gauss, is plotted in Fig. 55. The curve has a maximum at about 35 per cent. cobalt, and

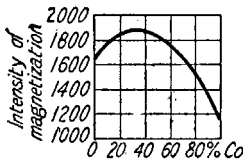


FIG. 55.—The Intensity of Magnetization of Cobalt-Iron Alloys.

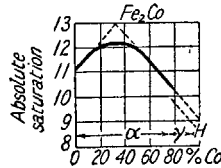
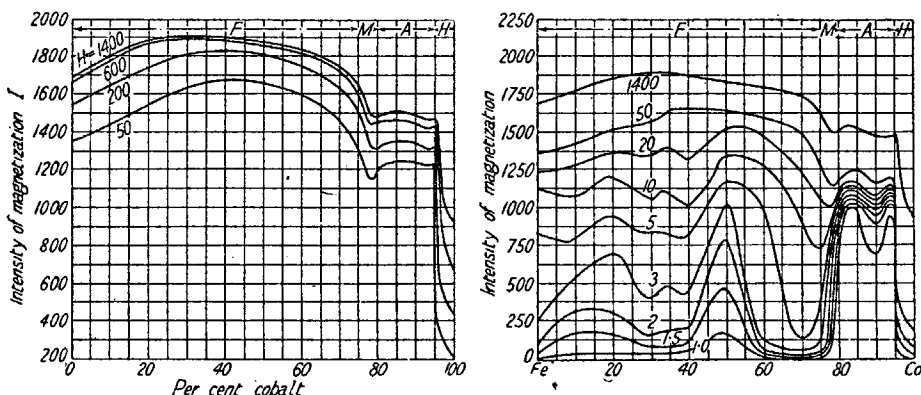


FIG. 56.—Saturation Capacity of the Cobalt-Iron Alloys.

this is in agreement with the results of A. Preuss, who found that with alloys near  $\text{Fe}_2\text{Co}$ , the saturation capacity is 10 per cent. greater than that of iron; and P. Weiss



and R. Forrer found that alloys with 35 to 45 per cent. of cobalt have a saturation capacity 12.4 per cent. greater than iron. Their results are summarized in Fig. 56, where at low temp., alloys with up to 78 per cent. of cobalt have a body-centred cubic lattice— $\alpha$ -ferrocobalts; those with 78 to 95 per cent. cobalt have a face-centred cubic lattice— $\gamma$ -ferrocobalts; and those with 95 to 100 per cent. cobalt, a hexagonal lattice of maximum density— $H$ -ferrocobalts. It is considered curious that the intensity of magnetization of an alloy—35 per cent. cobalt—is considerably greater than that of its components when it is remembered that the two elements form a continuous series of solid soln., and no compound. In other analogous cases, the saturation value of magnetization follows the additive rule, varying linearly from one component to another, as found by O. Bloch for the nickel-cobalt alloys. H. Masumoto represented the intensity of magnetization of the iron-cobalt alloys by the curves, Figs. 57 and 58, where F represents ferrite; M, martensite; A, austenite; and H, the alloys with the close-packed, hexagonal lattice. The numbers in Figs. 57 and 58 refer to the strength of the magnetic field in gauss.

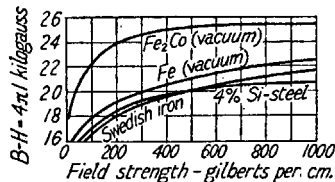
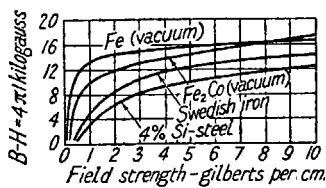


FIGS. 57 and 58.—The Intensity of Magnetization of the Iron-Cobalt Alloys.

The alloys of the  $\alpha$ - and  $\gamma$ -solid soln. are easily magnetized; the latter, especially has a high maximum permeability comparable with that of permalloy; the solid soln., with the close-packed, hexagonal lattice, is less magnetizable. The magnetization reaches a maximum with about 35 per cent. cobalt. K. Honda said that the true saturation value for iron is probably 2000, much greater than the commonly accepted value, 1700. In that case, the value 1700 is not the magnetic moment of one mol. multiplied by the number of mols. in unit vol., but merely the saturation value practically attainable. The maximum in the curve, Fig. 56, then, means that when iron is alloyed with about 35 per cent. of cobalt, the attainable saturation value for iron is raised, and made to approach the true saturation value. P. Weiss found that the alloy with about 29 per cent. of cobalt, corresponding with  $\text{Fe}_2\text{Co}$ , has a magnetic saturation value 10 per cent. greater than that of soft iron at ordinary temp., and he considered this as evidence of the formation of a cobalt diferride,  $\text{Fe}_2\text{Co}$ , analogous to the assumed nickel diferride,  $\text{Fe}_2\text{Ni}$ . T. D. Yensen obtained about 3 per cent. increase in the magnetization of these alloys when they are melted in vacuo. T. D. Yensen's results are summarized in Figs. 59 and 60; and for G. W. Elmen's results, see the cobalt alloys. Observations were made by O. von Auwers and H. Kühlewein, A. Kussmann and co-workers, T. Spooner, S. J. Barnett and L. J. H. Barnett, T. H. Gant, H. E. Kershaw, W. Oertel, R. L. Sanford, W. C. Ellis, E. H. Schulz and co-workers, F. Stäblein, R. L. Dowdell, J. F. Kayser, J. H. Partridge, S. Evershed, E. Gumlich, J. R. Gier, J. W. Shih, and E. A. Watson. P. Weiss and R. Forrer studied the saturation magnetization of the iron-cobalt alloys between ordinary temp. and the temp. of liquid air.

P. Weiss and R. Forrer found that the magnetization curve consists of two

straight lines connected by a curved portion, one curve slopes upwards from 0 to 13 per cent. of cobalt, and the other downwards from 50 to 78 per cent. of cobalt. The stable form of the alloy is a body-centred cubic lattice— $\alpha$ -ferrocobalt; from 78 to 95 per cent. of cobalt, the lattice is face-centred— $\gamma$ -ferrocobalt; and from 95 to 100 per cent. cobalt, the lattice is hexagonal. The magnetization curve in the region of



FIGS. 59 and 60.—Magnetization Curves of Iron and Iron-Cobalt Alloys.

$\gamma$ -ferrocobalt is linear. The magnetic moment of cobalt in the region  $\alpha$ -ferrocobalt rich in iron, is 17, but with the  $\alpha$ -ferrocobalt rich in cobalt, the magnetic moment of cobalt is 9, and iron 15; in  $\gamma$ -ferrocobalt, the magnetic moment of the cobalt is  $8\frac{3}{4}$ . For R. Forrer's observations on the two Curie points, *vide* iron; A. Guilbert studied the hysteresis; H. Kühlewein, the Curie points; R. Forrer, the magnetic moment of the alloys; and N. S. Akuloff, the anisotropy of cobalt.

H. T. Kalmus and K. B. Blake reported that the alloy corresponding with  $\text{Fe}_2\text{Co}$  has a saturation value of magnetization from 10 to 13 per cent. higher than that for iron alone; the higher values were obtained with samples prepared in vacuo, and are free from indications of a lack of cohesion. The best castings show a maximum permeability of approximately 13,000 at a density of 8000 gauss.\* This is considerably lower than the corresponding value for iron alone, but much greater than that of standard transformer steel. The most important property of the  $\text{Fe}_2\text{Co}$ -alloy is its permeability in medium fields—that is, for a magnetizing force of 50 to 200 gilberts per cm. Through this range, the permeability of the  $\text{Fe}_2\text{Co}$ -alloy is approximately 25 per cent. greater than that of iron alone or of commercial grades of transformer steel or iron. The hysteresis loss of the  $\text{Fe}_2\text{Co}$ -alloy is considerably less than for the best grades of commercial transformer steel at densities of 10,000 gauss, and about the same as for commercial iron at corresponding densities—about 15,000 gauss. C. F. Burgess and J. Aston observed that if the hysteresis loss per cycle with iron alone is unity, that with an alloy with 1.035 per cent. of cobalt is 1.20, and with 47.08 of nickel, 0.53. T. D. Jensen said:

The chief importance of cobalt lies in its magnetic permeability at high densities. An increase here of 25 per cent., when coupled with a low hysteresis loss, is a highly desirable characteristic, for instance, for the teeth of the armatures of dynamo machinery, where the density is always very high. Without going into detail, a few considerations will make this apparent. By increasing the density in the teeth 25 per cent.—which is allowable by using the  $\text{Fe}_2\text{Co}$ -alloy—the armature may be shortened a corresponding amount. As the increased density in the teeth necessarily means an increase in the density of the air-gap, the latter may be shortened so as to keep the field ampere turn for the air-gap and the teeth the same as before. Furthermore, the inside diameter of the armature core may be increased so as to give a smaller core cross-section. The shortening of the armature also shortens the pole pieces, and if a high permeability alloy is used in the field magnetic circuit as well as in the armature, the cross-section of the field core and yoke may also be reduced. From the above reasoning, it follows that the armature, besides requiring less iron, will also require less copper; and the field spools, while containing the same number of ampere turns as before, will also require less copper. The total reduction of iron and copper may thus amount to as much as 25 per cent. each. Passing from the required amount of material to the energy losses in the machine, the  $I^2R$  loss is reduced in direct proportion to the reduction in copper used. Furthermore, as the hysteresis loss is lower per pound for the  $\text{Fe}_2\text{Co}$ -alloy than for ordinary iron, and as the eddy current loss is about the same, the total core loss should be considerably less than with ordinary iron, in spite of the increased density. Thus, it would appear possible with this iron-cobalt alloy to construct dynamo machinery considerably lighter than at present, and with a higher efficiency.

K. Honda and K. Kido measured the magnetostriction of cobalt-iron alloys and observed an expansion with alloys with up to 10 per cent. of cobalt; a contraction with alloys having 90 per cent. or more; and alloys with 80 per cent. of cobalt gave an expansion, for fields up to  $\frac{H}{t}=300$  or 400 gauss, and a contraction with more intense fields. Y. Masiyama found that the longitudinal magnetostriction, Fig. 61, is the reverse of the transverse effect. The abrupt change with alloys near 80 per cent. of cobalt for both the longitudinal and transverse effects, corresponds with the change from the  $\alpha$ - to the  $\gamma$ -lattice. The change in vol. is the differential effect of the longitudinal and transverse changes in length. Observations were made by S. R. Williams.

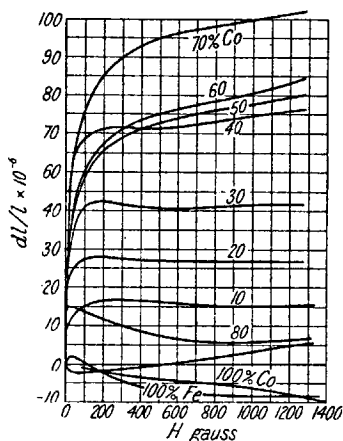


FIG. 61.—The Effect of the Magnetic Field on Magnetostriction.

about six times greater than it is with carbon steels; and the change in the rigidity is about four times greater than that of the elasticity.

The favourable effects of cobalt in hindering rusting were demonstrated by H. T. Kalmus and K. B. Blake. F. H. Mason, and H. Kirscht studied the effect

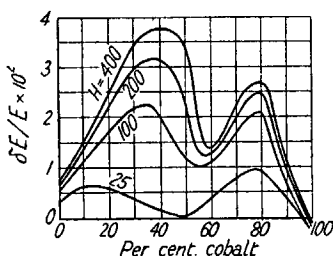


FIG. 62.—The Effect of Magnetization on the Elastic Modulus of Cobalt-Iron Alloys.

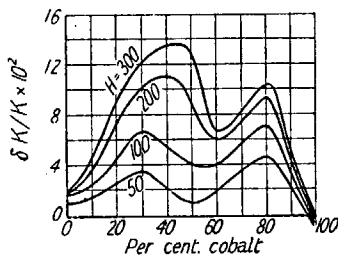


FIG. 63.—The Effect of Magnetization on the Rigidity of Cobalt-Iron Alloys.

of cobalt on the oxidation of iron. C. F. Burgess and J. Aston observed that when cobalt-iron alloys were exposed to the weather for 162 days from July to February, the losses by corrosion, expressed in kilograms per sq. metre per year; and the losses in grams per sq. cm. when immersed in 20 per cent. sulphuric acid for 1 hour, were as follow:

Cobalt	1.035	2.000	4.055	5.052 per cent.
Atmospheric corrosion	0.239	0.342	0.205	0.205
H <sub>2</sub> SO <sub>4</sub> -corrosion	0.705	1.020	0.356	0.257

W. Guertler and T. Liepus found that a 1 : 1-cobalt-iron alloy was attacked in less than 8 hrs. by 10 and 50 per cent. nitric acid; 10 and 36 per cent. hydrochloric acid; aqua regia; 10 per cent. sulphuric acid sat. with sodium sulphate;

carbon dioxide and air; acetic acid; citric acid; tartaric acid; chlorine water; sea-water; sea-water and air; rain-water and air; and a soln. of magnesium chloride. It was not attacked by a 10 per cent. soln. of sodium sulphide in 48 hrs., but a 50 per cent. soln. attacked it in less than 8 hrs.; it was attacked in 8 hrs. by a mixture of 4 per cent. sodium sulphide and 8 per cent. alkali. It was not attacked by a 50 per cent. soln. of sodium hydroxide in 8 hrs., or by a 10 per cent. soln. in 48 hrs., but in the presence of hydrogen dioxide the alloy was attacked. Aq. ammonia—10, 50, and 70 per cent.—had no perceptible action during 48 hrs. A 1:500-soln. of mercuric chloride was not stable in contact with the alloy. The action of these reagents on cobalt-iron-molybdenum alloys in the proportions 10:60:30, 40:40:20, and 60:10:30 was also examined. The corrodibility of the cobalt steels was studied by J. Stodart and M. Faraday, R. Mallet, W. D. Richardson, H. T. Kalmus and K. B. Blake, and O. Bauer and E. Piwowsky. C. F. Burgess and J. Aston exposed plates of iron-cobalt alloys for 162 days from July to February, and expressed the loss in kgrms. per sq. metre per year, and also to the action of 20 per cent. sulphuric acid for 1 hr. and expressed the loss in grams per sq. dm. per hour. The results were:

Cobalt	.	.	.	.	1.035	2.000	4.055	5.052 per cent.
Air	.	.	.	.	0.239	0.342	0.205	0.205
Acid	.	.	.	.	0.705	1.020	0.356	0.257

S. Endo's results, plotted in Fig. 64, represent the corrosion—loss in grms. per sq. cm.—during 5 hrs. action at ordinary temp. with alloys having 0.45 to 0.52 per cent. of carbon and:

Co	.	.	.	.	.	.	.	.
	2.01	4.80	10.25	19.40	30.01	39.90	50.50	per cent.
Loss { $H_2SO_4$	.	0.01154	0.00720	0.00214	0.00130	0.00094	0.00043	0.00047
{ $HCl$	.	0.00941	0.00532	0.00369	0.00152	0.00116	0.00072	0.00062
{ $HNO_3$	.	0.02768	0.02062	0.01302	0.02253	0.00156	0.00130	0.00130

Observations were also made by L. Aitchison. D. Saito and H. Okawa studied the nitridization of cobalt steels. J. H. Long and co-workers, and H. Remy and H. Gönningen studied contact catalysis of the  $2H_2 + O_2$  reaction by the alloy.

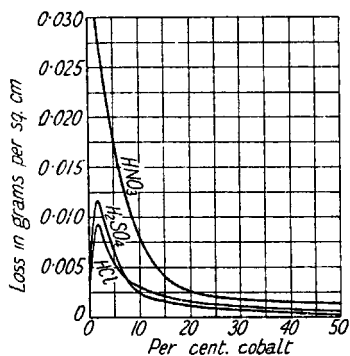


FIG. 64.—The Action of Acids on Cobalt-Steels.

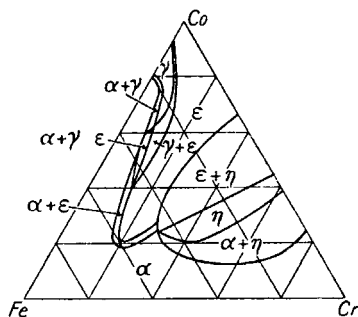


FIG. 65.—Phase Equilibria in the Cobalt-Iron-Chromium Alloys.

T. Bergman<sup>15</sup> made some **copper-iron-cobalt alloys** with the idea of obtaining a product resembling nickel. O. Dony-Hénault studied the corrosion of these alloys.

W. Köster studied the **iron-cobalt-aluminium alloys**. J. Pomey and P. Voulet, F. M. Ostraga, T. H. Gant, E. Hughes, F. Roll, E. A. Watson, L. Guillet, J. F. Kayser, E. H. Schulz and W. Jenge, and F. Wever and U. Haschimoto studied the **cobalt-iron-chromium alloys**—the observations of W. Köster are summarized in Fig. 65. K. Honda found that the alloy 36.5 per cent. iron, 5.54

per cent. cobalt, and 9 per cent. chromium has a coeff. of thermal expansion in the annealed state of  $10^{-7}$ , and another alloy very near this in composition has the negative coeff. of  $-1.2 \times 10^{-6}$ ; and these alloys are so resistant to corrosion that they have been called *stainless invar*. H. Masumoto studied the alloy. W. Oertel and F. Pölguter, W. Köster and W. Tonn, and W. Köster, studied **cobalt-iron-molybdenum alloys**. H. J. French and T. G. Digges, A. Michel and P. Bénazet, T. D. Yensen, L. L. Wyman and F. C. Kelley, W. Köster, P. W. Bridgman, B. A. Rogers, W. Köster and W. Tonn, and E. Houdremont and H. Schrader studied the **cobalt-iron-tungsten alloys**; K. Honda and S. Saito, W. Oertel and E. Pakulla, and L. Guillet, **cobalt-iron-chromium-tungsten alloys**; and E. Gumlich, and W. Köster and W. Schmidt, the **cobalt-iron-manganese alloys**.

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## § 10. Cobalt Suboxide and Monoxide

As in the case of iron, there are three well-defined oxides—cobalt monoxide, or cobaltous oxide,  $\text{CoO}$ ; cobaltous oxide,  $\text{Co}_3\text{O}_4$ ; and cobaltic oxide,  $\text{Co}_2\text{O}_3$ . A number of intermediate oxides have been reported, but their individuality has not been established. An unstable cobalt dioxide,  $\text{CoO}_2$ , is also known. I. L. Bell<sup>1</sup> suggested that some cobalt suboxide, perhaps  $\text{Co}_2\text{O}$ , is formed when cobaltous oxide is heated to  $327^\circ$  in a current of carbon monoxide; and when spongy cobalt is heated to dull redness in a current of carbon monoxide. This evidence of the existence of a suboxide is of no value; nor could S. Burgstaller confirm the existence of cobalt suboxide, whilst P. H. Emmett and J. F. Schultz, T. Vorster, G. Gallo, and L. Wöhler and O. Balz considered that it is not probable that the alleged suboxide is a chemical individual; and G. Natta and M. Strada found that the X-radiograms of the alleged cobalt suboxide are like those of mixtures of cobalt and its monoxide.

**The preparation of cobalt monoxide.**—As indicated in connection with the chemical properties of cobalt, compact cobalt does not readily oxidize in air at ordinary temp., but at a red-heat, the metal is slowly oxidized to the monoxide and afterwards to cobaltous oxide; at a higher temp., cobalt burns with a red incandescence. L. Wöhler and O. Balz found that the oxide obtained by burning cobalt in oxygen contained cobalt monoxide enclosing cobalt which oxidizes only

slowly, and hence the mixture gives rise to the impression that cobalt suboxide is produced. The finely-divided metal, reduced by hydrogen at a low temp., was found by G. Magnus<sup>2</sup> to be pyrophoric; and the metal reduced at a red-heat was found by H. Hess gradually to take up oxygen. E. Donath also found that spongy cobalt, obtained by reducing at a low temp., is oxidized in air; W. G. Mixter noted that at 12 to 13 atm. press., cobaltous and cobaltosic oxides are formed; and H. T. Kalmus observed that cobalt obtained by reducing the oxide in carbon monoxide at 600° is oxidized if withdrawn hot from the furnace. H. P. Walmsley observed that the oxide is formed when cobalt is electrically spluttered in air. P. H. Emmett and J. F. Schultz obtained the oxide by blowing oxygen into molten cobalt. G. C. Winkelblech obtained cobalt monoxide by roasting the powdered metal in air, and also by heating cobaltous hydroxide below 350° in a current of hydrogen, and by calcining the hydroxide or carbonate in air. W. Beetz employed a similar process.

J. L. Proust observed that if cobaltosic oxide be vigorously calcined it forms the monoxide, and H. Moissan obtained the monoxide by heating cobaltosic oxide in the oxyhydrogen flame. C. D. Braun recommended a red-heat; and J. A. Hedvall, H. T. Kalmus, H. Moissan, 1000°. The transformation of cobaltosic to cobaltous oxide occurs at 900° to 1000°, and the product readily takes up oxygen when cooled in air. W. J. Russell heated cobaltosic oxide in a current of carbon dioxide, and cooled the resulting monoxide in the same gas; and C. R. A. Wright and A. P. Luff, E. von Sommaruga, R. Schneider, P. Hausknecht, W. Hempel and H. Thiele, and H. Remmler used a similar process. J. L. C. Zimmermann employed carbon dioxide, and also nitrogen for the inert gas.

H. W. Foote and E. K. Smith heated cobaltosic oxide in vacuo at 970°, and then 3 hrs. at 1000°, and pumped off the oxygen. T. W. Richards found that at a red-heat, in vacuo, cobaltosic oxide yields cobaltous oxide, cobalt, and some higher oxide. M. le Blanc and E. Möbius, G. Natta and M. Strada, W. J. Russell, and G. C. Winkelblech obtained cobalt monoxide by heating the hydroxide in vacuo, or in an inert gas—nitrogen or carbon dioxide; L. Wöhler and O. Balz recommended working at 500° to 600°; and G. Natta and A. Reina, at 200°. T. W. Richards and G. P. Baxter recommended the following procedure:

From the soln. of the metal in nitric acid the pink, granular, cobaltous hydroxide was precipitated by adding an excess of freshly re-distilled ammonia, and subsequently digesting the mixture upon the steam bath in a platinum bowl. This precipitate was collected upon a Gooch crucible in which a circular piece of hardened filter-paper was used instead of an asbestos mat. After drying and converting the mass into the black oxide by ignition with an alcohol lamp, the product was heated to full redness in a boat contained in an evacuated porcelain tube until the weight of the oxide remained constant within 0.1 mgrm.

J. E. Möbius observed that this mode of preparation is not to be recommended, because of the difficulty in dealing with adsorbed oxygen, and he said that the monoxide is best obtained by precipitating cobaltous carbonate from a soln. of cobalt nitrate by the addition of sodium carbonate; and, since the precipitate is very easily oxidized by atm. oxygen, in alkaline soln., the operation should be conducted in an atm. of nitrogen. T. W. Richards and G. P. Baxter themselves said: "With great reluctance the work on cobalt monoxide was abandoned . . . for a substance whose composition varies so widely under conditions which vary so slightly is obviously unfitted for work of the highest accuracy in atomic weight determinations." S. Prasad and co-workers recommended heating the carbonate to 900°.

In view of the fact observed by M. le Blanc and J. E. Möbius, that cobaltous oxide readily absorbs oxygen to form  $\text{CoO} \cdot n\text{O}_2$ , or else  $\text{Co}_3\text{O}_4$ , it is an open question if the earlier workers ever obtained pure cobaltous oxide. F. Glaser obtained the monoxide by heating cobaltosic oxide in hydrogen at 215° for 8 hrs., and H. T. Kalmus recommended 300°. P. H. Emmett and J. F. Schultz recommended a similar process. H. Moissan heated trihydrated cobaltic oxide in hydrogen at

190° to 200°. I. L. Bell, and L. Wöhler and O. Balz found that the product approximates in composition to the suboxide when cobaltous oxide is heated in carbon monoxide at 419° to 630°.

According to H. T. Kalmus, if cobaltous oxide is heated with 2 or 3 per cent. of carbon at 900°, it forms a yellowish-green cobaltous oxide which he considered to be an allotropic variety of the ordinary oxide—apparently because the oxide prepared at that temp. is grey. The evidence is not sufficient to justify the assumption of allotropy—as usually defined.

T. Vorster, and C. Winkler observed that cobaltic oxide heated in ammonia at 350° forms brownish-yellow cobalt monoxide, and, at a higher temp., the metal. C. M. Loane obtained the oxide for use as a catalyst by the low temp. oxidation of the pyrophoric metal.

C. F. Bucholz obtained what he regarded as cobaltous oxide by heating the nitrate at a red-heat for 1 hour, and then at a white-heat for half an hour; S. Burgstaller said that the decomposition is completed at 750° to 760° in consequence of the reducing action of flame gases; and H. von Wartenberg and W. Gurr added that the decomposition is complete at 1200°. According to F. Bedford and E. Erdmann, when a hot soln. of cobaltous nitrate is treated drop by drop with soluble organic compounds like the carbohydrates, and tartaric acid, finely-divided cobaltous oxide is formed. V. M. Goldschmidt and co-workers heated a mixture of cobalt chloride with sodium carbonate and leached out the alkali; E. L. Reakirt heated cobaltic chloropentamminochloride; M. Lachaud and C. Lepière obtained the oxide, mixed with higher oxides, by the ignition of the sulphate; J. J. Setterberg, G. C. Winkelblech, J. E. Möbius, W. Beetz, and W. J. Russell, by the rapid ignition of the carbonate at a red-heat; H. Rose heated the basic carbonate at 150° in a covered crucible; and F. Emich, S. Holgersson, S. Holgersson and A. Karlsson, P. Hausknecht, and W. G. Mixter heated the carbonate in an atm. of carbon dioxide or nitrogen. The absorption of oxygen by heated cobaltous oxide is illustrated by the experiments of M. le Blanc and J. E. Möbius on the decomposition of cobaltous carbonate, and bringing in oxygen, at different temp.:

Calced at	300°	320°	420°	460°	1050°	300°	420°	450°
Oxygen at	18°	18°	18°	18°	18°	400°	250°	250°
Excess oxygen	6.4	4.63	2.14	1.93	Trace	9.99	7.76	6.65
	Only CoO					Only Co <sub>3</sub> O <sub>4</sub>		

The higher the temp. of calcination, the less is the amount of oxygen adsorbed. H. Copaux heated cobalt oxalate in a closed vessel, and obtained cobaltous oxide mixed with cobalt; and P. Riban obtained a similar product by heating a 5 per cent. soln. of cobalt formate in vacuo at 175°; and C. D. Braun obtained the oxide by heating cobaltic nitroxypentamminoxalate; and H. V. Regnault found that when cobalt is heated in steam, cobalt monoxide is formed. L. Wöhler and O. Balz observed that the reaction with finely-divided cobalt proceeds quickly, and with sintered cobalt the speed of the reaction is measurable at a red-heat. F. Emich, and P. Sabatier and J. B. Senderens observed that cobalt monoxide is formed when the metal is heated to 150° in an atmosphere of nitric oxide.

A. Schwarzenberg, and M. Ferrières and E. Duport obtained octahedral crystals of the monoxide by the action of steam on heated cobaltous chloride. A. C. Becquerel reported crystals of the monoxide to be formed by heating a mixture of cobaltic oxide with an excess of potassium hydroxide in a silver crucible, and after cooling the fused mass, washing the product with water. A. Schwarzenberg added that the product is potassium cobaltite. J. J. Ebelmen obtained octahedral crystals by heating cobalt borate with lime in a porcelain oven, and washing away the soluble products with cold hydrochloric acid; and A. Duboin, by adding potassium chloride to a fused mixture of potassium hydrofluoride and cobalt oxide or chloride; keeping the mixture at a red-heat for 2 or 3 days; and washing the cold mass with

water. W. Florence observed that octahedral crystals of the oxide are formed in the borax bead; and H. Grandeau, by heating a mixture of cobalt phosphate and potassium sulphate. V. Kohlschütter and J. L. Tüscher prepared an **aerosol** of the oxide.

The cobalt oxides of commerce have no definite composition, but the superfine cobalt oxide, branded FEKO, approximates  $\text{CoO}$ , and has 77 to 78 per cent. of metal; grey cobalt oxide, GKO, approximates  $\text{Co}_3\text{O}_4$ , and has 75 to 76 per cent. of metal; prepared cobalt oxide, FKO, approximates  $\text{Co}_3\text{O}_4$ , and 72 to 74.5 per cent. of metal; black cobalt oxide, SKO, approximates  $\text{Co}_2\text{O}_3$ , and about 70 per cent. of metal; and black cobalt oxide, RKO, approximates  $\text{Co}_2\text{O}_3$  and has 66 to 68 per cent. of metal.

According to A. Weissenborn, the oxide prepared by precipitation with hypochlorites contains up to 2 and in some cases 5 per cent. of nickel; and H. T. Kalmus gave for the composition of the commercial oxide:

Co	Ni	Fe	S	As	CaO	$\text{SiO}_2$ (or insolubles)
70.36	1.12	0.82	0.45	0.10	0.50	0.20 per cent.
69.20	1.40	0.50	0.54	—	0.37	1.46 „

with traces of silver. The subject was discussed by O. Barth, W. A. Lampadius, G. Selve, and E. W. von Siemens and J. G. Halske. The sulphur may be present as calcium sulphate, and it can be purified from sulphur by boiling with a soln. of sodium carbonate, washing out the sodium sulphate, and removing the calcium carbonate with dil. hydrochloric acid. H. T. Kalmus thus reduced the sulphur from 0.45 to 0.020 per cent., and the calcium from 0.50 to 0.021 per cent. B. Bogitch removed the sulphur by heating the oxide with wood charcoal—sugar charcoal does not answer, presumably because of the absence of alkali carbonates. E. A. E. Weinberg purified the cobalt by converting it into chloride, volatilizing the chloride, and then oxidizing the chloride. F. Feigl and H. I. Kapulitzas say that all the nickel can be removed as follows:

The soln. is treated with a conc. soln. of potassium cyanide until the precipitate first formed just re-dissolves, an excess of hydrogen dioxide is added to convert the cobalto-into cobalti-cyanide, and the soln. is evaporated to one quarter its volume to destroy the excess of peroxide. On addition of dimethylglyoxime to the hot soln. followed by formaldehyde until its odour is apparent in the soln., the nickel is precipitated as the characteristic red glyoxime compound together with excess of the precipitant; the compound is purified by dissolution in hydrochloric acid and precipitation in the usual way. The method is based on the reaction  $\text{K}_2\text{Ni}(\text{CN})_4 + 2\text{H}.\text{CHO} = \text{Ni}(\text{CN})_2 + 2\text{CN}.\text{CH}_2.\text{OK}$ . The nickel-free filtrate is evaporated to dryness and the carbon removed by roasting; the washed residue is dissolved in conc. hydrochloric acid, and the cobalt hydroxide precipitated by potassium hydroxide; the well-washed residue is then calcined for oxide.

**The properties of cobaltous oxide.**—J. L. Proust described cobaltous oxide as a greenish-grey powder; G. C. Winkelblech, as an olive-green powder; W. J. Russell, a pale brown powder; C. D. Braun, a black powder; and J. A. Hedvall, dark red. P. Riban observed that when precipitated from the formate, the colour is rose-red. H. B. Weiser observed a grey- and a red-coloured oxide, due, probably, to differences in the size of the grain. Strongly-heated cobaltous oxide is dark blue, and when this is ground the colour becomes paler, and finally appears to be dark grey. O. C. M. Davis and F. W. Rixon discussed the relation between the colour and the heat of formation. M. Lachaud and C. Lepierre, M. Ferrières and E. Duport, J. J. Ebelsen, H. Grandeau, A. C. Becquerel, J. A. Hedvall, and W. Florence described the octahedral, isotropic crystals, and which belong to the cubic system. The habit is tabular, or acicular. The X-radio-graphs show that the crystal lattice is of the sodium chloride type. G. Natta and co-workers, and F. M. Bravo said that the cubic, face-centred lattice has four molecules per unit cell; V. M. Goldschmidt and co-workers, and G. Lunde gave  $a=4.254 \text{ \AA}$ ; F. M. Bravo,  $4.32 \text{ \AA}$ . H. P. Walmsley,  $4.247 \text{ \AA}$ ; and S. Holgersson and A. Karlsson,  $a=4.262 \text{ \AA}$ . Observations were made by J. A. Hedvall.

P. P. Ewald and C. Hermann gave 4.25 Å. as the best representative value. V. M. Goldschmidt obtained 2.14 Å. for the distance between the cobalt and oxygen atoms in the lattice. G. Natta and M. Strada's X-ray spectral lines of cobaltous oxide are indicated in Fig. 66. O. Hahn and O. Müller studied the surface of cobalt oxide from observations on the absorbed radium emanations. L. Passerini studied the solubility. J. J. Ebelmen gave 6.52 for the sp. gr. of crystals of cobalt monoxide;

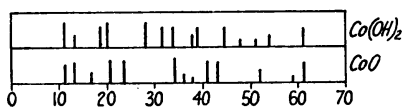


FIG. 66.—X-ray Spectral Lines of Cobaltous Oxide and Hydroxide.

M. Lachaud and C. Lepière, 6.7; A. Du-boin, 6.05; and L. Playfair and J. P. Joule gave 5.597 for the oxide, and after ignition, 5.750. G. Natta and A. Reina, and M. le Blanc and J. E. Möbius gave 6.62; and S. Holgersson gave 6.47 at 18°. For the sp. gr. calculated from the space-lattice, F. M. Bravo gave 6.538; G. Natta and

A. Reina, 6.62; G. Natta and M. Strada, 6.22; S. Holgersson, 6.45; and H. P. Walmsley, 6.455. A. Baladin studied the contraction which occurs during the formation of cobaltous oxide from its elements. G. Bruni and A. Ferrari discussed the solid soln. C. Zengelis said that vaporization can be detected at ordinary temp., but this statement has not been confirmed. M. Watanabe said that the dissociation press. of the oxide at 25° is  $4.46 \times 10^{-72}$  mm. of mercury. According to H. Moissan, cobaltous oxide melts when heated rapidly in the electric-arc furnace, and the cold cake is a mass of reddish crystals. H. Wartenberg and co-workers gave 1935° for the m.p.; P. L. Dulong gave for the heat of formation  $(\text{Co}_2\text{O}_3) = 63.8$  Cals.; M. Bertholet, 64.1; J. Thomsen,  $(\text{Co}_2\text{O}_3, \text{H}_2\text{O}) = 63.4$  Cals. W. A. Roth and H. Havekoss gave  $(\text{Co}_2\text{O}_3) = 57.2$  Cals. for the heat of formation of cobaltous oxide. G. Chaudron gave 61.1 Cals. M. Watanabe gave  $\delta Q = -55,768$  cals., and  $-50,626$  cals. for the free energy at 25°. W. G. Mixter gave  $(\text{Co}_2\text{O}_3) = 57.587$  Cals. for the crystalline oxide, and 50.5 Cals. for the amorphous oxide, and P. H. Emmett and J. F. Schultz calculated 56.154 Cals. at 25°. W. Biltz, and G. Chaudron made observations on the subject. R. von Dallwitz-Wegener, G. Beck, and P. H. Emmett and J. F. Schultz calculated values for the free energy; and M. Watanabe gave 14.46 cal. per degree for the entropy at 25°. O. C. M. Davis and F. W. Rixon studied the reaction between the colour and the heat of formation. G. K. Burgess and R. G. Waltenburg measured the emissivity of the oxide for red-light, and B. Monasch found that the radiation of light from a cobaltous oxide electrode in the electric arc is very small. A. Wehnelt said that the oxide is inactive so far as the emission of electrons is concerned when the oxide is fixed on a platinum disc and used as the cathode of a discharge tube. M. Kimura and M. Take-waki found that cobalt oxide absorbs ultra-violet light. F. Jentsch studied the emission of electrons by the oxide. M. le Blanc and H. Sachse gave  $10^{-3}$  ohm for the electrical conductivity at 18°, and E. Friederich said that it is non-conducting. W. Meyer also measured the conductivity of the oxide. W. Beetz said that the oxide is non-magnetic; and E. H. Williams, that it is ferro-magnetic. P. Hausknecht gave  $67 \times 10^{-6}$  mass unit for the magnetic susceptibility, and E. F. Herroun and E. Wilson,  $74.5 \times 10^{-6}$ . F. Merck and E. Wedekind studied the subject; and Y. Kato and T. Takei prepared magnets from the oxide. W. Klemm and W. Schüth found that the mol. magnetic susceptibility,  $\chi \times 10^6$ , of cobaltous oxide prepared by calcining the carbonate, was:

H (gauss)	at 500°			at 600°			at 800°		
	20°	190°	440°	20°	215°	250°	20°	220°	440°
765	10,300	9590	8640	9740	8700	8010	9000	7860	7260
1510	9,810	9060	7950	9300	8310	7510	8920	7860	7040

G. C. Winkelblech, and H. Kunheim observed that the olive-green powder turns brown in air; and W. J. Russell, and J. L. C. Zimmermann, that the brown powder is stable in air, but M. le Blanc and J. E. Möbius found that the oxide prepared

by heating the carbonate in vacuo at  $350^\circ$ , becomes black and takes up oxygen on exposure to air until its composition approximates  $\text{Co}_3\text{O}_4$  without changing its lattice structure. Most observers—*e.g.* W. Beetz, F. Glaser, W. A. Lampadius, W. G. Mixter, H. Moissan, H. Rose, and W. J. Russell—have noted the passage of cobaltous oxide into cobaltosic or an intermediate oxide when it is calcined in air. According to H. W. Foote and E. K. Smith, and J. Hagenacker, the dissociation pressure of oxygen with cobaltous oxide at  $1100^\circ$  is not perceptible, although T. W. Richards and G. P. Baxter said that the dissociation pressure of the oxide at  $800^\circ$  is 1.5 mm. of mercury. This shows that the oxide contained some absorbed oxygen. M. le Blanc and J. E. Möbius found the dissociation press. at  $1250^\circ$  is less than  $0.00013$  atm. P. H. Emmett and J. F. Schultz calculated the partial press. of oxygen over cobaltous oxide at  $1100^\circ$  to be  $6.6 \times 10^{-11}$  atm.; L. Wöhler and O. Balz calculated the dissociation press. at  $450^\circ$ ,  $6.02 \times 10^{-29}$  atm.; and at  $747^\circ$ ,  $6.02 \times 10^{-19}$  atm.; and W. Biltz observed 0.046 atm. at  $2477^\circ$ ; 0.17 atm. at  $2627^\circ$ ; 0.80 atm. at  $2827^\circ$ ; 1.58 atm. at  $2927^\circ$ ; and 2.24 atm. at  $2977^\circ$ . In the oxidation of cobalt in air, cobaltosic oxide is formed between  $300^\circ$  and  $431^\circ$ , and at  $869^\circ$ , solid soln. of cobaltosic oxide and cobalt monoxide are formed. A. A. Read found that the oxide lost all its oxygen when heated in the tip of the oxy-coal gas flame at, say,  $1750^\circ$ . P. Schützenberger observed that at a white-heat, in nitrogen, cobaltous oxide loses in weight about 0.4 per cent. Cobalt monoxide, said H. Moissan, is one of the most stable of the oxides at a high temp. C. M. Despretz studied the reduction of cobalt oxide by **hydrogen** at a red-heat, and W. J. Russell, J. L. C. Zimmermann, and H. Remmler, by the flame gases in a crucible over a Bunsen burner. The direct formation of cobalt by the reduction of the oxide was studied by E. Emich, G. Gallo, W. Müller, H. Remmler, W. J. Russell, C. Winkler, and J. L. C. Zimmermann; L. Wöhler and O. Balz, and G. Gallo observed no intermediate formation of a suboxide (*q.v.*). According to C. R. A. Wright and A. P. Luff, the reduction of cobalt monoxide in hydrogen begins at about  $165^\circ$ , W. Müller said at  $197^\circ$ , H. T. Kalmus, and H. Moissan,  $250^\circ$ ; and F. Glaser,  $228^\circ$ , and he added that reduction is complete at  $500^\circ$  to  $600^\circ$ . G. Gallo observed that the reduction of cobaltous oxide begins at about  $118^\circ$  to  $120^\circ$ , but metallic cobalt is obtained only after 4 hrs. at  $400^\circ$ , 3 hrs. at  $500^\circ$ , 1 hr. at  $600^\circ$ , and 15 mins. at  $700^\circ$ . No sign of a cobaltous suboxide appears as an intermediate stage of the reduction. C. M. Despretz observed that the temp. at which cobalt monoxide is reduced by hydrogen is the same as that at which the metal is oxidized by steam. For the balanced reaction:  $\text{CoO} + \text{H}_2 \rightleftharpoons \text{Co} + \text{H}_2\text{O}$ , see cobalt. L. Wöhler and O. Balz observed that the equilibrium constant for the reaction:  $\text{CoO} + \text{H}_2 \rightleftharpoons \text{Co} + \text{H}_2\text{O}$ , is  $K = [\text{H}_2\text{O}]/[\text{H}_2]$ , or  $K = 13.5$  at  $450^\circ$ . G. Chaudron studied the reaction, and obtained  $K = 20$  at  $1020^\circ$ . P. H. Emmett and J. F. Schultz, and M. Watanabe found that the equilibrium constants,  $K = [\text{H}_2\text{O}]/[\text{H}_2]$ , in the reaction at different temp., are:—

	$450^\circ$	$515^\circ$	$570^\circ$	$570^\circ$	$1000^\circ$
$K$ . . . . .	63.2	52.7	45.8	31.3	21.1

The free energy of the reaction is  $-3678$  cal. at  $25^\circ$ . There is no evidence of the formation of solid soln. of cobaltosic and cobaltous oxides, and this is confirmed by the X-radiograms. Z. Shibata and I. Mori gave for the reaction:  $\text{CoO} + \text{H}_2 = \text{Co} + \text{H}_2\text{O}$ , the free energy  $-5450$  cal. at  $25.1^\circ$ ; for the heat of the reaction,  $-57,820$  cal.; and  $\log K = 494.1917 - 1 + 1.08690$ . W. J. Russell, and T. W. Richards and G. P. Baxter said that cobalt monoxide is but slightly hygroscopic, and that during several weeks' exposure to **air** it absorbed no perceptible oxygen, and after 8 to 9 months' exposure, only traces of a higher oxide were formed. P. Schützenberger added that it does not occlude **oxygen** so readily as nickel monoxide. J. E. Möbius showed that the grain-size of the monoxide prepared in vacuo depends on the temp. of preparation, and that the in-take of oxygen by the monoxide depends on the grain-size, and temp. M. le Blanc and J. E. Möbius showed that when cobaltous oxide takes up oxygen at  $18^\circ$ , the crystal lattice does not change,

but if the oxygen is absorbed at  $100^{\circ}$  or upwards, the cobaltous oxide lattice is formed and shows that the unstable  $\text{CoO} \cdot n\text{H}_2\text{O}$  formed by absorption, passes into the stable  $\text{Co}_3\text{O}_4$ . The change is rapid at  $400^{\circ}$ . The absorbed oxygen in  $\text{CoO} \cdot n\text{O}$  is either interstitial oxygen (13. 66, 17) or else it is adsorbed on the surface. If the oxide be slowly cooled in air, W. J. Russell, and C. D. Braun observed that a higher oxide is formed. J. L. C. Zimmermann showed that if the oxide be heated in air on a piece of platinum foil, a black higher oxide is formed—according to H. Moissan, as the temp. is raised, the sequence of changes is :  $\text{CoO} \rightarrow (\text{Co}_3\text{O}_4 \rightarrow) \text{Co}_2\text{O}_3 \rightarrow \text{Co}_3\text{O}_4 \rightarrow \text{CoO}$ . J. Hagenacker observed that when cobaltous oxide is heated in oxygen above the dissociation press. of cobaltous oxide, there is an absorption of oxygen by the cobaltous oxide between  $1050^{\circ}$  and  $1150^{\circ}$ . H. Moissan, and E. Frémy observed that some cobaltic oxide is formed when cobalt monoxide is heated in air. H. Rose found that the monoxide is insoluble in **water**. S. S. Bhatnagar and S. L. Bhatia studied the rate of evaporation of adsorbed water from the surface of the oxide ; and A. Quartaroli, and F. G. Tryhorn and G. Jessop, the catalytic action of **hydrogen dioxide**.

R. Wasmuth observed that cobaltous oxide is attacked by **chlorine** at about  $250^{\circ}$ , and at  $550^{\circ}$  the reaction is faster—and the presence of carbon favours the attack by chlorine. G. Gore observed that dry **hydrogen fluoride** does not act on the oxide below  $0^{\circ}$ . H. Rose, and J. L. C. Zimmermann found that the oxide is readily dissolved by dil. **hydrochloric acid**, forming a rose-red soln., and in the conc. acid, forming a deep blue soln. A. Ducelliez studied the action of cobaltous oxide on **hypochlorites**—see 1. 8, 4. J. L. C. Zimmermann found that the oxide dissolves slowly in the cold in **perchloric acid**, and rapidly when heated. Cobalt monoxide dissolves in acids to form cobaltous salts. For example, according to C. F. Bucholz, F. A. C. Gren, J. A. Hedvall, H. Kunheim, W. A. Lampadius, J. L. Proust, P. Schwarzenberg, and J. A. Hedvall, the solubility of the oxide in hydrofluoric, hydrochloric, perchloric, sulphuric, nitric, phosphoric, and arsenious acids which occurs slowly at ordinary temp., and more rapidly at a high temp., forms rose-red soln. ; conc. hydrochloric and sulphuric acids form blue soln. J. L. Proust, and J. J. Setterberg found that cobalt sulphide is formed when cobalt oxide is heated with **sulphur** ; and H. Rose said that when heated with sulphur, cobalt sulphide and sulphur dioxide are produced, and, according to O. Schumann, cobalt oxysulphide is also formed. J. B. Senderens observed that with sulphur in the presence of water, cobalt sulphate and thiosulphate are formed ; and when the mixture is boiled, cobalt sulphate is formed—no thiosulphate. J. J. Ebelmen observed that at a red-heat, **hydrogen sulphide** converts cobaltous oxide into sulphide. H. Rose observed that hydrogen sulphide converts it into cobalt sulphide and water. O. Schumann added that at ordinary temp., water, sulphur, and oxysulphide are formed. C. Matignon and F. Bourion found that at  $400^{\circ}$ , a mixture of chlorine and sulphur monochloride converts cobaltous oxide into the chloride. The oxide dissolves slowly in cold, dil. **sulphuric acid**, but more quickly in the hot acid. C. Dufraisse and D. Nakae studied the catalytic action on soln. of sodium sulphite.

G. Gore, and E. C. Franklin and C. A. Kraus found that cobaltous oxide is insoluble in liquid **ammonia** ; and E. Divers, that it is insoluble in ammonia with some ammonium nitrate in soln. T. Vorster, C. Winkler, and L. Santi observed that cobalt oxide is reduced to metal when it is heated in a current of ammonia, and some ammonium nitrate is formed. S. Hauser represented the effect of temp. on the press. at constant vol., time constant, and the effect of time on the press. at constant temp., by Fig. 67. J. L. Proust, and F. A. C. Gren said that the oxide is slightly soluble in aq. ammonia, but their results may have been due to the peptization of the oxide by the ammonia, because L. Gmelin, H. Rose, and J. L. C. Zimmermann said that the oxide is insoluble in that menstruum. J. L. C. Zimmermann observed that cobaltous oxide is not changed by a hot soln. of ammonia of sp. gr. 0.95. If air or oxygen has access, cobaltous oxide was found

by J. L. Proust, and G. C. Winkelblech to dissolve in aq. ammonia. E. Frémy, and L. Brugnatelli discussed the formation of ammines. M. F. Fogler discussed the preparation of a cobalt oxide-alumina catalyst for the oxidation of ammonia. R. H. Brett found that cobalt monoxide is insoluble in soln. of **ammonium chloride or nitrate**, but H. Rose said that it dissolves in a hot soln. of ammonium chloride, and F. A. C. Gren, and J. L. C. Zimmermann added that as the oxide dissolves, ammonia is evolved, and a soln. of cobalt chloride is formed. L. Santi found that at an elevated temp., dry ammonium chloride reduces cobalt oxide to the metal. J. L. Proust, and F. A. C. Gren observed that the oxide is soluble in a soln. of **ammonium carbonate**. The oxide also dissolves in a soln. of **ammonium thiocyanate**. F. Emich found that **nitric oxide** converts it into cobaltous oxide. H. Rose, and J. L. C. Zimmermann observed that cobalt monoxide is readily dissolved by dil. or conc. nitric acid; a cold or hot acid of sp. gr. 1.315 readily dissolves the oxide. R. Weber found that **phosphorus pentachloride** reacts vigorously with heated cobaltous oxide to form cobaltous and phosphoryl chlorides. H. Bassett and H. S. Taylor observed that **phosphoryl chloride** acts on cobaltous oxide at ordinary temp., and at 100° forms anhydrous cobaltous chloride, and in a soln. of ethyl acetate the reaction results in the formation of a complex salt of cobaltous chloride and ethyl acetate.

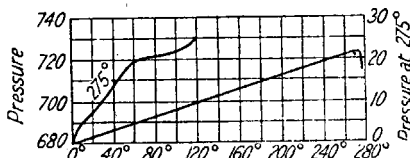


FIG. 67.—The Reduction of Cobalt Oxide by Ammonia.

T. Vorster found that cobalt oxide is readily reduced to the metal when it is heated with **carbon**, and C. R. A. Wright and A. P. Luff added that the reduction begins at 450°. The reaction with carbon was studied by G. Tammann and A. Y. Sworykin, and R. Berger and L. Delmas; and the reduction of the oxide by coal, and by wood charcoal, by B. Bogitch. T. Vorster observed that the oxide is reduced by **carbon monoxide**. C. R. A. Wright and A. P. Luff, and F. Glaser found that the reaction with carbon monoxide begins at 115°, and with carbon at about 450°; and I. W. Fay and co-workers, with carbon monoxide at 140°. F. Fischer and co-workers studied the formation of carbides in this reaction. M. Watanabe found the equilibrium constant,  $K = P_{\text{Co}_2}/P_{\text{CO}}$ , for the reaction:  $\text{CoO} + \text{CO} \rightleftharpoons \text{Co} + \text{CO}_2$ , and found it ranges between 174.4 at 563° and 23.2 at 861°; M. Watanabe gave for the heat of the reaction,  $-11,544 - 3.5T + 0.00305T^2 - 0.062T^3$ ; and for the free energy,  $-11,544 + 8.06T \log T - 0.00305T^2 + 0.031T^3 - 17.65T$ . F. Merck and E. Wedekind, Z. Shibata and I. Mori, B. Bogitch, P. H. Emmett and J. F. Schultz, and G. Chaudron studied the reaction. A. Laurent observed that a mixture of equal vols. of carbon monoxide and dioxide reduces cobalt oxide to the metal, and it has no action on cobalt itself. K. Fujimura studied the reduction of carbon monoxide by the cobalt oxide catalyst associated with other oxides. H. Hollings and R. H. Griffith studied the adsorption of hydrocarbons by the oxide. P. Sabatier, and P. Sabatier and P. Mailhe observed that at about 200°, **alcohol** is oxidized by cobaltous oxide to aldehyde; P. Cambouives found that **carbon tetrachloride** at 550° converts cobaltous oxide into chloride, and A. Michael and A. Murphy found that in a sealed tube at 100°, a soln. of chlorine in carbon tetrachloride converts cobaltous oxide into chloride. H. Rose, J. L. C. Zimmermann, and F. A. C. Gren observed that **acetic acid** and **tartaric acid** dissolve the oxide slowly in the cold, and more rapidly when heated; the monoxide is also attacked by **oxalic acid** slowly in the cold, rapidly when heated to form insoluble cobalt oxalate. Oxalic acid forms a cobaltous salt, and any adsorbed oxygen oxidizes the oxalic acid very slowly. H. Bodenbender found that a litre of a soln. containing 418 grms. of **sugar** and 34.3 grms. of lime, dissolves 1.56 grms. of cobalt oxide, and 0.29 grm. when 296.5 grms. of sugar and 2.42 grms. of lime are present. J. Aloy



and C. Rabaut noted that the oxide favours the hydrolysis of the **cyanohydrins**. C. Dufraisse and D. Nakae studied the catalytic oxidation of **acraldehyde**, **benzaldehyde**, **furfuraldehyde**, **styrene**, and **turpentine**. According to J. Aloy and A. Valdiguié, **hydroquinone**, in a soln. containing ammonium chloride, is

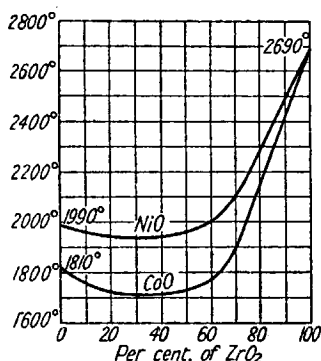


FIG. 68.—Fusion Curves of Mixtures of Zirconia with Nickel and Cobalt Oxides.

oxidized, particularly when warmed on a water-bath. M. Rüger observed no combination with **silica** between  $900^{\circ}$  and  $1200^{\circ}$ . Cobalt oxide forms a silicate when heated with silica; J. F. Shepherd studied the system:  $CoO-Fe_2O_3-SiO_2$ ; and M. Billy and M. A. Foex, the solubility of the oxide in fused **glasses**. J. A. Hedvall, S. Holgersson and A. Herrlin, and L. Passerini found that cobalt oxide forms a titanate with **titanium dioxide**, but no compound was observed by J. A. Hedvall, or by H. von Wartenberg and W. Gurr, with **zirconia**; or by J. A. Hedvall, or by S. Burgstaller, with **thoria**. H. von Wartenberg and H. J. Reusch represented the m.p. of mixtures of zirconia and cobalt oxide by the curve, Fig. 68.

According to J. L. Gay-Lussac and L. J. Thénard, and C. M. Despretz, **potassium** and **sodium** readily reduce the oxide to metal. F. A. C. Gren said that a little cobaltous oxide is dissolved by dil. soln. of **alkali hydroxides**, and J. L. C. Zimmermann said that none is dissolved. For the action of alkali hydroxides on cobaltous oxide, *vide infra*, cobaltic oxide. H. Rose, C. Winkler, E. Donath, and J. L. C. Zimmermann observed that cobaltous oxide is soluble in a conc. soln. of alkali hydroxides, forming intense blue liquids, which were studied by A. Völker, A. Remelé, and E. Donath. The monoxide is insoluble in a soln. of **potassium carbonate**. According to J. Persoz, cobaltous oxide is soluble in a boiling soln. of cerium and nickel nitrates with the precipitation of the oxides. J. J. Berzelius observed that when heated on charcoal, with sodium carbonate, the oxide is readily reduced to metal in the inner blowpipe flame. The indefinite products obtained by heating **beryllium oxide** with cobalt oxide were discussed by J. A. Hedvall, J. J. Berzelius, and C. F. Plattner. The solid soln. furnished by mixtures of **magnesium oxide** and cobalt oxide—including the so-called **magnesia-red**—were discussed by J. J. Berzelius, J. A. Hedvall, S. Holgersson and A. Karlsson, L. Passerini, G. Natta and L. Passerini, and K. A. Hofmann and K. Höschel. Solid soln. are formed when mixtures of cobalt oxide and **calcium oxide** are heated to a high temp.; and they were studied by J. A. Hedvall, G. Natta and L. Passerini, H. J. Reusch and H. von Wartenberg, R. Schenck, and R. Schenck and H. Wesselkock; and J. A. Hedvall, and R. Schenck obtained similar results with **strontium oxide**, and with **barium oxide**. J. A. Hedvall and N. von Zweigbergk studied the action of **barium peroxide**. J. A. Hedvall also studied the reactions with **barium**, **strontium**, and **calcium sulphates**. The so-called *Rinman's green*, *zinc green*, *Saxon green*, and *cobalt green* is produced by calcining mixtures of **zinc oxide** and cobalt oxide—see percobaltites for bibliography. The solid soln. was studied by S. Burgstaller, J. A. Hedvall, and G. Natta and L. Passerini; and the absorption spectrum by R. Hill and O. R. Howell. No chemical combination was observed by J. A. Hedvall, and L. Passerini when mixtures of **cadmium oxide** and cobalt oxide are calcined. J. A. Hedvall, W. Biltz and co-workers, and H. von Wartenberg and H. J. Reusch studied the m.p. of mixtures of **alumina** and cobalt oxide; and S. Izawa, the luminescence of the mixtures. J. A. Hedvall, G. Natta and L. Passerini, M. Rüger, S. Bleekrode, R. Hill and O. R. Howell, and J. G. Gentele discussed the formation of cobalt orthostannate—called *blue céleste*, *caruleum*, or *eldest blue*—when a mixture of **stannic oxide** and cobalt oxide is heated together;

and J. J. Berzelius, J. A. Hedvall, A. Ditte, and G. Natta and L. Passerini obtained cobalt metastannate similarly. J. A. Hedvall observed no evidence of the formation of a solid soln. or of compound with **lead oxide**. F. de Carli observed that at 250° to 300°, **lead dioxide** oxidizes cobalt oxide to a higher oxide. J. A. Hedvall studied the products with **chromic oxide**—*vide* chromites. J. A. Hedvall, S. Holgersson and A. Karlsson, G. Natta and L. Passerini, R. Schenck, and R. Schenck and H. Wesselkock observed the formation of solid soln. when cobalt oxide and **manganous oxide** are heated together; and J. A. Hedvall, A. Gorgeu, and M. Salinger observed that with **manganese dioxide**, permanganites are formed. S. Holgersson and A. Karlsson, S. B. Hendricks and W. H. Albrecht, G. Natta and M. Strada, S. Veil, J. A. Hedvall, and L. Passerini observed that with **ferric oxide**, a ferrite,  $\text{Co}(\text{FeO}_2)_2$ , is formed; and solid soln. are formed with **nickel oxide**. J. A. Hedvall studied the action of cobalt oxide on numerous **metal oxides** at 1100° and 1300°. No compounds were observed when cobalt oxide is heated to about 1100° with copper, calcium, strontium, barium, beryllium, magnesium, zinc, and cadmium oxides—*vide infra*, cobaltites. A blue aluminate,  $\text{CoO} \cdot \text{Al}_2\text{O}_3$ , is formed with **alumina** at 1100°, and at a higher temp., a green aluminate,  $4\text{CoO} \cdot 3\text{Al}_2\text{O}_3$ . The product—*Thénard's blue*—was studied by L. J. Thénard, J. A. Hedvall, G. Natta and L. Passerini, S. Burgstaller, S. Holgersson, M. Rüger, J. J. Ebelman, R. J. Elliot, R. K. Goselitz, P. Louyet, G. Pokrowsky, R. Schenck and H. Wesselkock, R. Hill and O. R. Howell, and W. Stein. G. Natta and L. Passerini, and J. A. Hedvall observed that no compounds are formed with **lanthanum oxide**, or with **cerium dioxide**. A green chromite,  $\text{CoO} \cdot \text{Cr}_2\text{O}_3$ , is formed with **chromic oxide**; a green tantalate with **tantalum pentoxide**, and likewise with **columbium pentoxide**; a green vanadate, with **vanadium pentoxide**; and a yellow uranate with **uranium trioxide**; Q. C. Montemartini and A. Vernazza studied the action on soln. of **chromic sulphate**.

**The preparation of cobaltous hydroxide.**—J. L. Proust,<sup>3</sup> W. Beetz, and G. C. Winkelblech showed that when potash-lye is added to a soln. of a cobaltous salt, out of contact with air, a blue precipitate is first formed, this becomes violet, and finally rose-red. The changes are accelerated by a rise of temp. If the soln. of the cobalt salt be poured into the boiling potash-lye, the change in colour is very rapid. When cobaltous carbonate is boiled with the potash-lye, the cobaltous hydroxide first produced appears as a voluminous, blue mass which afterwards becomes violet and ultimately rose-red.

L. J. Curtman and A. D. S. John found that the precipitate can be detected in a soln. of cobaltous nitrate containing 1 part of cobalt in 80,000 parts of soln. H. T. S. Britton, and H. T. S. Britton and R. A. Robinson titrated electrometrically, at 18°, 100 c.c. of a 0.0247*M*-soln. of cobaltous chloride with 0.0900 *N*-NaOH, and the results are shown in Fig. 69. Precipitation began when the e.m.f. was 0.676 volt,  $P_H=6.81$ , and when 0.9 c.c. of the soln. of sodium hydroxide had been added, and 54.8 c.c. were theoretically required. B. Schragar noted that cobaltous hydroxide shows acidic and basic properties. According to E. Frémy, W. N. Hartley, and W. Traube and B. Loewe, the washed precipitate retains alkali very tenaciously, and hence baryta water has been recommended as a precipitant, followed by washing with hot water; and L. Thompson, and J. L. C. Zimmermann recommended mercuric oxide as precipitant. G. C. Winkelblech emphasized the importance of removing the air from the soln. of cobalt salt and the potash-lye by boiling before they are mixed, since, as shown by J. L. Proust, the moist hydroxide

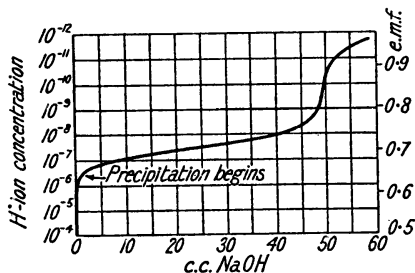


FIG. 69.—The Electrometric Titration for Cobalt Hydroxide.

rapidly changes its colour in air owing to the formation of cobaltic hydroxide. S. Kern noted cobaltous hydroxide is formed when magnesium acts on a conc. soln. of a cobaltous chloride—hydrogen is at the same time evolved; S. E. Moody; as an intermediate product when a soln. of cobaltous sulphate is hydrolyzed in the presence of potassium iodide and iodate; R. Saxon, when a soln. containing cobalt sulphate is electrolyzed; W. J. Russell, when cobaltous carbonate is hydrolyzed by water; and A. Girard, when cobaltous arsenate is hydrolyzed by hot potash-lye.

As indicated above, the blue hydroxide was obtained by J. L. Proust when a cobaltous salt soln. is treated with aqua ammonia, or alkali-lye in the absence of air. According to W. Beetz, W. A. Lampadius, J. L. Proust, A. Remelé, W. J. Russell, C. W. Stillwell, and G. C. Winkelblech, the formation of the blue hydroxide is favoured by a low alkalinity of the soln., and a low temp. A. Hantzsch recommended using less than the theoretical proportion of alkali-lye; and A. Bernardi found that the optimum proportion of cobalt salt to alkali is 1 : 0.02. G. Hüttig and B. Kassler, and R. Kassler recommended the following procedure for preparing the blue hydroxide :

A soln. of 22 grms. of potassium hydroxide in 300 grms. of water is added drop by drop to a soln. of 50 grms. of hexahydrated cobaltous nitrate dissolved in 1000 grms. of water, in an atmosphere of coal-gas, at 0°. The blue precipitate is washed by decantation ten times with 5 litres of air-free water; and dried over sulphuric acid in a desiccator. The product is free from alkali and nitrates. The blue colour of the washed precipitate becomes less marked, and this is not due to the presence of impurities, or to oxidation.

The observations of W. Beetz, F. Feigl, E. Frémy, F. Gauhe, N. R. Dhar, A. Hantzsch, T. Katsurai, J. L. Proust, A. Remelé, C. W. Stillwell, and G. C. Winkelblech showed that the formation of the rose-red hydroxide is favoured by a high alkalinity, and a high temp. G. F. Hüttig and R. Kassler, and R. Kassler prepared the pink hydroxide as follows :

A soln. of 40 grms. of potassium hydroxide in 500 grms. of water is dropped into a soln. of 40 grms. of hexahydrated cobaltous nitrate in an atm. of coal-gas, at 0°, and the rose-red precipitate is washed with water on a filter, and dried in a desiccator over sulphuric acid. A. Hantzsch washed the precipitate, in an atm. of hydrogen, by hot water, then with alcohol, and ether, and dried it in vacuo. G. Natta and co-workers washed the precipitate successively with water, alcohol, and ether, and then dried it at 80° in an atm. of nitrogen.

W. Beetz said that the blue precipitate first formed is a basic salt; but A. Hantzsch observed that when it is precipitated from a soln. of the sulphate by an insufficient quantity of alkali, and washed with cold water until no more sulphuric acid is removed, the residue always contains much sulphate. Repeated boiling with water free from air, however, gradually removes most of the sulphate without altering the blue colour. The red hydroxide is obtained by precipitating with an excess of alkali, washing with hot water in an atmosphere of hydrogen, and finally washing with alcohol and ether. It retains some water even after prolonged heating in nitrogen at 300°, whilst the blue hydroxide is completely dehydrated at 170°; on the other hand, acetyl and benzoyl chlorides react much more vigorously with the red than with the blue compound. The case is regarded as one of "chromo-isomerism," and the formulæ  $\text{Co}(\text{OH})_2$  and  $\text{H}_2\text{O} \dots \text{CoO}$  are suggested for the red and blue compounds respectively. The blue precipitation was studied by E. Donath, H. Ditz, F. Reichel, C. Winkler, and C. Tubandt—*vide infra*, hydrated cobaltic oxides. S. R. Benedict found that the change from blue to rose-pink is retarded by the presence of a small amount of nickel salt, and he supposed that the deep blue of nickel cobaltite masks the rose-pink of cobaltous hydroxide. H. B. Weiser added that increasing amounts of nickel salt do not increase the intensity of the blue colour, so that the effect is more likely to be due to the stabilization of the blue hydroxide by nickel hydroxide. The presence of the sulphates of iron(ous), zinc, manganese, magnesium, chromium, copper, and

aluminium; the chlorides of tin and calcium; and the nitrates of lead, cadmium, thorium, and strontium were found by N. G. Chatterji and N. R. Dhar to produce no marked effect. J. A. Hedvall found both the blue and rose-pink precipitates are gelatinous, but apparently pass into microcrystalline forms on standing. H. B. Weiser suggests that the precipitated hydrated oxide is most finely-divided when first formed and thus appears blue; but in the presence of a slight excess of alkali, the highly hydrated mass loses water and becomes denser, so that the colour at the same time changes from blue, through lavender, to rose. The rate of this transformation is hastened by raising the temp., and retarded or stopped by the presence of basic cobalt salts or nickel. H. J. Witteveen and E. F. Farnau noted the change from pink to blue if the pink hydroxide is allowed to stand in contact with cobalt salt soln.

The blue or green, gelatinous precipitate of cobaltous hydroxide even changes to a rose colour. G. C. Winkelblech suggested that the blue precipitate is a basic salt, and that the green colour is due to a partial oxidation. A. Hantzsch said that both the blue- and rose-coloured precipitates are hydrates of cobaltous oxide—one, the blue, is assumed to be  $\text{CoO} \cdot \text{H}_2\text{O}$ , and the other, the rose, is  $\text{Co}(\text{OH})_2$ . H. B. Weiser questioned this hypothesis, and attributed the variation in colour to a difference in the grain-size. C. W. Stillwell said that the rose-coloured precipitate is a stable crystalline form, whilst the blue one is amorphous and unstable. Blue is the colour by reflected light, green the colour by transmitted light. G. F. Hüttig and R. Kassler said that the X-radiograms show that both the blue- and the rose-coloured hydrates are crystalline, and that the difference in colour is solely due to grain-size—the blue-coloured one being the more finely-divided. H. B. Weiser and W. O. Milligan said that the X-radiograms show that the blue- and rose-coloured hydrates are crystalline, but that the crystalline forms are different. The blue and green have the same crystalline form, and they call it  **$\alpha$ -cobaltous hydroxide** to distinguish it from the rose-coloured or  **$\beta$ -cobaltous hydroxide**. The blue and green preparations owe their difference in colour to a difference in physical character. The green is the colour by transmitted light and the blue is probably a reflected colour, a Tyndall blue (C. W. Stillwell).  $\alpha$ - $\text{Co}(\text{OH})_2$  is the unstable form. In the presence of alkali, the  $\alpha$ -form dissolves and reprecipitates as the less soluble, stable  $\beta$ -modification. The  $\alpha$ - to  $\beta$ -transformation can be prevented or retarded by the presence of strongly adsorbed substances in the soln. from which the  $\alpha$ -form precipitates. The blue form is stabilized indefinitely by small amounts of mannitol, sorbitol, dulcitol, sucrose, lactose, maltose, xylose, arabinose, raffinose, galactose, and dextrose. The transformation is retarded by cobalt salts (A. Hantzsch); by  $\text{Ni}(\text{OH})_2$  simultaneously precipitated (S. R. Benedict); and by albumin, gelatin, and sulphates. The adsorption is strong even with soln. of relatively low concentration, as would be expected from the marked stabilizing action of the compounds. The order of adsorption is: lactose > maltose > sucrose > raffinose. The peptizing action of the sugars as a result of adsorption on hydrous ferric oxide (A. Dumansky) follows the same order. Cobaltous hydroxide in contact with a soln. of cobaltous chloride undergoes colour transformations from green to blue to lavender. The blue and green substances are mixtures of  $\alpha$ - $\text{Co}(\text{OH})_2$ ,  $\beta$ - $\text{Co}(\text{OH})_2$ , and a basic salt  $\text{CoCl}_2 \cdot 3\text{CoO} \cdot 3 \cdot 5\text{H}_2\text{O}$ . The lavender compound formed on long standing is the pure basic salt.

A. de Schulten prepared crystals of the hydroxide by heating a mixed soln. of hydrated cobaltous chloride (10 grms.) in 60 c.c. of water, and 250 grms. of potassium hydroxide. When solution is complete, the vessel is allowed to stand for 24 hrs., and agitated, if necessary, in order to promote the separation of crystals. Crystals were also prepared by this process by P. Hausknecht; and M. le Blanc and J. E. Möbius, and J. E. Möbius added that the product is contaminated by much alkali, which can be removed by a protracted washing with water. They accordingly preferred to add 125 grms. of potassium hydroxide to a soln. of 10 grms. of hexahydrated cobaltous chloride in 30 grms. of water, in place of A. de Schulten's

mixture. R. Saxon obtained the hydroxide by the electrolysis of water with a cobalt anode.

T. W. Richards and G. P. Baxter, O. F. Tower and M. C. Cooke, and C. W. Stillwell observed that cobaltous hydroxide is peptized when it is repeatedly washed with water; and G. F. Hüttig and R. Kassler added that it is not so easily peptized as cobaltic hydroxide. C. Tubandt prepared **colloidal cobaltous hydroxide** by the anodic dissolution of cobalt in conc. alkali-lye, at a low current density, say 0.2 amp. per sq. dm., and at an elevated temp. The cobaltous hydroxide in soln. is precipitated by shaking with barium sulphate. The colloid does not dialyze. G. Grube and O. Feucht, however, showed that the blue soln. is due to the formation of potassium cobaltite, and not colloidal cobaltous hydroxide. The blue alkaline soln. of cobaltous salts containing glycerol, studied by F. Reichel, are also thought to be hydrosols of cobaltous hydroxide. S. Prakash and N. R. Dhar, N. G. Chatterji and N. R. Dhar, H. Colin and A. Sénéchal, and K. C. Sen and N. R. Dhar studied the peptization of the hydroxide by sucrose, dextrose, *lævulose*, galactose, lactose, mannose, dextrin, starch, and glycerol. H. B. Weiser suggested that the hydroxide may not be colloidal in glycerol soln. L. Hugouneng and J. Loiseleur employed glycogen as protective colloid; and A. Dumansky and B. Saprometoff, sodium tartrate, or mannite. A. Müller prepared a colloidal soln. by peptizing the precipitated hydroxide—hydrogel—with a dil. mineral acid. The hydroxide is shaken up in a flask with water, and the acid or salt soln. added in successive portions until a clear liquid is obtained. The mixture should be well boiled after each addition. O. F. Tower and M. C. Cooke prepared the colloidal soln. by dialyzing a soln. of cobalt tartrate in the presence of an alkaline soln. of potassium tartrate; and O. F. Tower, by the action of alcoholic *N*-KOH on a soln. of cobalt acetate in glycerol. N. R. Dhar and S. Ghosh, and K. C. Sen and N. R. Dhar peptized cobaltous oxide with alkali-lye. C. Paal and H. Boeters, and Kalle and Co. prepared colloidal soln. from soln. of the sulphate, using the fission products of albumin (protalbates, lysalbates, alkali albumoses, etc.) as protective colloids, and dialyzing the liquid. F. E. Lloyd and V. Moravek, and Wo. Ostwald and K. Popp obtained rhythmic rings of cobaltous hydroxide by pouring aq. ammonia on a gelatin gel containing cobaltous chloride. In some cases a spiral is obtained instead of rhythmic bands. They were studied by N. G. Chatterji and N. R. Dhar. A. and E. Lottermoser studied the ageing of the hydroxide.

**The properties of cobaltous hydroxide.**—Analyses of cobaltous hydroxide, by J. L. Proust, W. Beetz, G. C. Winkelblech, and L. Schaffner, agree with the formula  $\text{Co}(\text{OH})_2$ . G. C. Winkelblech said that cobaltous hydroxide is a rose-red powder, and W. Beetz added that the brownish tinge observed by J. L. Proust is due to aerial oxidation to cobaltic hydroxide. C. W. Stillwell observed that freshly-precipitated cobaltous hydroxide is green to yellowish-green by transmitted light, and is gelatinous, laminar, amorphous, and metastable. The blue colour is essentially a reflected colour; it is probably a Tyndall blue scattered by small crystal nuclei which form within the amorphous matrix as the gelatinous precipitate ages to the crystalline form. The freshly-precipitated hydroxide tends to change to the rose-coloured hydroxide, which is granular in appearance and is the stable, crystalline form. No other crystalline forms were produced; the light blue, aged precipitate is crystalline, but it has the same structure as the rose-coloured hydroxide. The blue of the aged precipitate is also structural. Adsorbed cobalt chloride inhibits crystal growth, favours the formation of the green precipitate, and hinders that of the rose. Freshly-precipitated nickelous hydroxide is laminar and amorphous, and tends to stabilize the corresponding amorphous cobalt hydroxide. The change from green to blue of freshly-precipitated cobaltous hydroxide is not due to oxidation. For the blue due to oxidation, *vide infra*, hydrated cobaltic oxides. If a soln. of cobaltous chloride is added to potash-lye in amounts greater than the mol. ratio 1 : 1.5, and the precipitate is allowed to remain in contact with the mother-liquor, ageing occurs and the colour of the

precipitate changes from green to blue to rose; the final rose-coloured precipitate is a basic salt of cobalt and is the only crystalline product formed under the experimental conditions; the blue is a mixture of the rose and the green; and the green is amorphous, containing small amounts of crystalline hydroxide and basic salt.

The deep-violet powder obtained by A. de Schulten consists of microscopic, brownish-red, elongated rhombic prisms grouped in needles; but G. Natta and co-workers showed that the crystals are trigonal. A. de Schulten said that the crystals are pleochroic, being rose-red along *a*, rose-yellow along *b*, and pale brownish-yellow along *c*. The double refraction is about 0.04. The X-radiograms of the crystals were found by G. Natta and co-workers to correspond with a uniaxial, rhombohedral lattice having  $a=3.19$  Å., and  $c=4.66$  Å., or  $a:c=1:1.46$ . There is one molecule per unit cell. G. Natta and M. Strada's X-ray spectral lines of the hydroxide are shown in Fig. 71. V. M. Goldschmidt and co-workers discussed the subject.

The X-radiograms of cobalt and nickel hydroxides simultaneously precipitated show that the two compounds are isomorphous. The sp. gr. calculated from the space-lattice data is 3.75. A. de Schulten found 3.597 at 15°. The hydroxide loses water when heated over 100°, and the colour becomes green or black. In an inert gas, or in vacuo, as shown by M. le Blanc and J. E. Möbius, C. F. Bucholz, F. Gauhe, J. E. Möbius, G. Natta and M. Strada, W. J. Russell, B. M. Tassaert, L. J. Thénard, and G. C. Winkelblech, cobaltous oxide is formed. According to G. F. Hüttig and R. Kassler, and R. Kassler, the dehydration curves of blue and pink hydrated cobaltous oxides, at 10 mm. press., Fig. 70, show that with freshly-precipitated material, the water-content at first falls rapidly with rise of temp. until it contains about 1.5 mols. of water to each mol. of cobaltous oxide, after which it decreases slowly with rise of temp. up to 168°, when it has the composition  $\text{CoO} \cdot \text{H}_2\text{O}$  (approx.). At this temp. there is considerable loss of water at constant temp., the composition changing to about  $\text{CoO} \cdot 0.4\text{H}_2\text{O}$ , which again loses water steadily with rise in temp. At 300°, 0.1 mol. of water is still held by the cobaltous oxide. The difference between the rose and blue forms of hydrated cobaltous oxide is one of fineness of division only; the blue form is more finely-divided. The two forms have identical X-ray spectra, distinct from that of anhydrous cobaltous oxide. On heating either form with water, a more stable product, containing less water and showing the above phenomena to a much less marked extent, is formed. This stabilization is more rapid with the blue than with the rose form. T. Katsurai said that in an autoclave, under a press. of 20 atm., the hydroxide is not changed. J. Thomsen gave for the heat of formation ( $\text{Co}_2\text{O}_3, \text{H}_2\text{O}$ ) = 63.4 Cals., and for the heat of reaction with hydrogen sulphide ( $\text{Co}(\text{OH})_2, \text{H}_2\text{S} \cdot \text{H}_2\text{O}$ ) = 17.41 Cals. E. Peterson found the heat of neutralization with hydrofluoric acid to be 13.245 Cals.; J. Thomsen gave for the heat of neutralization with hydrochloric acid, 10.57 Cals.; with nitric acid, 10.546 Cals.; and with sulphuric acid,  $\frac{1}{2}\text{H}_2\text{SO}_4$  aq., 12.336 Cals. P. A. Favre and J. T. Silbermann obtained rather lower values. P. H. Emmett and J. F. Schultz calculated for the free energy,  $E$ , of the reaction  $\text{Co}_3\text{O}_4 + \text{H}_2 = 3\text{CoO} + \text{H}_2\text{O}$ , at 370°, 515°, and 800°, respectively, -39.197, -36.539, and -44.717 Cals. Steam does not form cobaltous oxide when passed over cobaltous oxide at 500°. The ratios of steam to hydrogen necessary to oxidize the cobaltous oxide at 370°, 515°, and 800°, are, respectively,  $2.4 \times 10^{12}$ ,  $1.3 \times 10^{10}$ , and  $1.3 \times 10^9$ . H. W. Vogel studied the absorption spectrum of cobaltous hydroxide; F. Allison and E. J. Murphy, the magneto-optic properties; and G. Wiedemann, and S. Veil, the magnetic properties. A. Quartaroli gave  $40.6 \times 10^{-6}$  mass unit; and P. Hausknecht,  $140 \times 10^{-6}$  mass unit for the magnetic susceptibility.

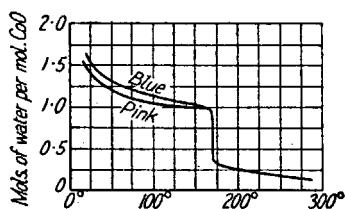


FIG. 70.—Dehydration Curves of Blue and Pink Hydrated Cobaltous Oxides.

Both the blue and rose-red hydroxides have absorption bands at  $640\text{m}\mu$  and  $585\text{m}\mu$ ; and there is complete absorption beyond about  $675\text{m}\mu$  in both cases; and there is also a band at  $560\text{m}\mu$  with the blue and at  $520\text{m}\mu$  with the rose-red form. Observations were made by W. J. Russell.

H. Copaux found that cobaltous hydroxide is attacked by hydrogen at  $375^\circ$  to  $380^\circ$ ; and G. F. Hüttig and R. Kassler, said that the reduction of the blue hydroxide occurs in 20 hrs. at  $300^\circ$ , and in 8 hrs. at  $550^\circ$ . A. de Schulten said that the crystals of cobaltous hydroxide are not altered by exposure to air; but, as observed by W. Beetz, A. Bernardi, J. J. Berzelius, F. Feigl, A. Hantzsch, G. F. Hüttig and R. Kassler, J. L. Proust, L. J. Thénard, G. C. Winkelblech, and J. L. C. Zimmermann, the fresh precipitate readily oxidizes in air and as the proportion of cobaltic oxide increases, the colour changes from blue to green, olive-green, and dirty brown. According to R. H. Brett, J. L. Proust, S. Kern, and J. B. Rogojsky, the hydroxide is very sparingly soluble, or insoluble in water, but G. Almkvist observed that a litre of water dissolves 3.18 mgrms. of cobalt hydroxide. H. T. S. Britton gave for the solubility product  $[\text{Co}^{++}][\text{OH}]^2 = 1.6 \times 10^{-18}$ . The oxidation of cobaltous hydroxide by hydrogen dioxide was studied by R. Fischer, A. H. McConnell and E. S. Hanes, and P. Pellini and D. Meneghini; the oxidation of cobaltous hydroxide by lead dioxide, by H. Rose, and O. W. Gibbs; and by other agents as indicated in connection with the higher oxides of cobalt. According to C. F. Bucholz, S. Kern, J. L. Proust, J. B. Rogojsky, A. de Schulten, C. W. Stillwell, B. M. Tassaert, O. F. Tower and M. C. Cooke, G. C. Winkelblech, and C. Winkler, C. Reichard found that the freshly-precipitated hydroxide in the cold and in contact with barium dioxide, turns grey, and finally black. The hydroxide readily dissolves in acids, forming salts.

J. L. Proust observed that cobaltous hydroxide is oxidized by chlorine water; and the action of electrolytic chlorine in alkaline soln. was studied by E. Hüttner. O. Ruff and W. Menzel showed that fluorine monoxide oxidizes cobaltous hydroxide, suspended in water, to form a peroxide. The action of potassium hypochlorite or hypochlorous acid on cobaltous hydroxide was studied by O. Popp, F. Field, C. D. Braun, A. Terreil, E. and B. Klimenko, A. Brochet, E. Mitscherlich, R. Böttger, T. Fleitmann, F. Stolba, and E. Hüttner—*vide infra*, cobalt dioxide. According to T. Döring, the cobalt hydroxide is oxidized, and some oxygen as well as potassium chloride and chlorate are formed. The proportion of cobaltous hydroxide can be made so small that the transformation of the hypochlorite cannot be effected by a purely chemical process; and the proportion of oxygen evolved does not depend on the proportion of cobalt oxide employed. Consequently, the cobalt hydroxide here acts as a catalytic agent. At  $100^\circ$ , in alkaline soln., oxygen and potassium chloride are formed, but no chlorate is produced. Hypochlorous acid at  $100^\circ$  furnishes oxygen and hydrochloric acid, and the latter may be partly oxidized to form chlorine and cobaltous chloride. With chlorine in alkaline soln. in the presence of cobalt hydroxide, the reaction is symbolized:  $2\text{Co}(\text{OH})_2 + 2\text{KOH} + \text{Cl}_2 = 2\text{Co}(\text{OH})_3 + 2\text{KCl}$ . Temperature is an important factor. With the theoretical proportion of chlorine in potash-lye, T. Döring found that at  $100^\circ$ , or a higher temp., oxygen and potassium chloride, free from chlorate, are formed. At a lower temp., only part of the oxygen of the hypochlorite initially formed is liberated, and the remaining part is present as hypochlorite mixed with chloride. When chlorine is bubbled into a soln. of alkali-lye, more hypochlorite may be formed than can be decomposed by the catalyst cobalt hydroxide, and when all the potash-lye has been transformed into hypochlorite, etc., F. Förster observed that some chlorate may be produced. At  $100^\circ$  or over, the more rapid catalytic action on the hypochlorite results in a reduced yield of chlorate. The formation of chlorate by the secondary action of chlorine on the unconverted hypochlorite was discussed by G. Lunge and L. Landolt, F. Oettel, F. Förster, and T. Döring. A. J. Balard observed the oxidation of cobaltous hydroxide by bromine. T. Döring found that when bromine or hypobromite acts on alkali-lye in the presence of cobalt

hydroxide, free oxygen and alkali bromate are formed. The primary action of bromine is to form a mixture of bromide, and hypobromite. When liquid bromine is added to the alkali-lye, the proportion of bromate formed depends on the conc. of the lye, whether the bromine or alkali-lye is in excess, and on the temp. If the bromine is introduced drop by drop, or in the state of vapour, a greater proportion of oxygen is evolved than when liquid bromine is employed. This is because the cobalt hydroxide has a greater chance of inducing the decomposition of the hypobromite to oxygen and bromide than is the case when the liquid bromine acts in a more concentrated form. The action of iodine and of hypiodites was studied by R. L. L. Taylor, T. Döring, and E. Hüttner. There is no development of oxygen, and the whole of the alkali which reacts with the iodine forms iodate, nor does potassium hypiodite furnish oxygen, and it is in this respect unlike the hypochlorite and hypobromite. S. E. Moody, and S. R. Benedict found that the hydroxide is oxidized by potassium iodate in accord with the equation:  $6\text{Co}(\text{OH})_2 + \text{KIO}_3 + 3\text{H}_2\text{O} = 6\text{Co}(\text{OH})_3 + \text{KI}$ .

J. B. Senderens found that when treated with sulphur and water, cobaltous hydroxide forms cobalt sulphate and thiosulphate. E. Hüttner represented the action of potassium persulphate on cobaltous hydroxide by the equation:  $2\text{Co}(\text{OH})_2 + \text{K}_2\text{S}_2\text{O}_8 + 2\text{H}_2\text{O} = 2\text{Co}(\text{OH})_3 + \text{K}_2\text{SO}_4 + \text{H}_2\text{SO}_4$ ; and similarly with ammonium persulphate. A. de Schulten said that the crystals are insoluble in aq. ammonia. R. H. Brett found that the hydroxide is soluble in soln. of ammonium salts—sulphate, chloride, nitrate, or succinate; but A. de Schulten found that the crystals are insoluble in a cold soln. of ammonium chloride, but soluble in a warm soln. H. Grössmann found that the hydroxide is soluble in a boiling soln. of ammonium thiocyanate. C. A. Wurtz found that the hydroxide is insoluble in methylamine and in amylamine. W. Traube and B. Löwe found that the hydroxide dissolves in ethylenediamine, and forms a complex salt. E. Saint-Evre studied the transformation of the hydroxide into  $\text{K}_3[\text{Co}(\text{NO}_2)_6] \cdot n\text{H}_2\text{O}$ , by the action of an excess of potassium nitrite. H. Rose found that hypophosphites, in the cold, form cobalt hypophosphite; and A. Hantzsch added that phosphoryl chloride reacts vigorously with the hydroxide. C. Reichard observed that the hydroxide is not changed by arsenic trioxide in alkaline soln.

F. and E. Rodgers found that cobaltous hydroxide is readily dissolved by a soln. of potassium cyanide. T. Döring observed that when cyanogen acts on alkali-lye in the presence of cobalt hydroxide, there is no formation of free oxygen. He showed that neither at ordinary temp. nor at  $100^\circ$  is there any development of gas when cobalt hydroxide acts on a soln. of potassium cyanate. In the reaction, J. von Liebig observed that when precipitated cobalt hydroxide stands in contact with a soln. of the cyanate, ammonium and potassium carbonates are formed. C. D. Braun studied the action of potassium ferricyanide; and D. Bhaduri and P. Ray represented the reaction:  $3\text{Co}(\text{OH})_2 + 2\text{KOH} + 2\text{K}_3\text{FeCy}_6 = \text{Co}_3\text{O}_4 + 4\text{H}_2\text{O} + 2\text{K}_4\text{FeCy}_6$ . A. de Schulten said that the crystals are soluble in warm dil. acetic acid; J. Spiller observed that the hydroxide is not precipitated by potassium hydroxide in the presence of citric acid, or ammonium citrate. A. Job, and W. Wernicke found that a soln. of sodium tartrate forms a violet soln. with cobalt hydroxide; and with a boiling soln. of the tartrate, a complex salt is formed. H. Rose, and F. Field observed that tartaric acid, and also citric acid hinder the precipitation of cobalt hydroxide from soln. of its salts by alkali hydroxides; and H. Ditz, C. Tubandt, and F. Reichel noted a similar result with glycerol—*vide supra*, colloidal cobaltous hydroxide. A. Dumansky and B. Saprometoff found that sodium tartrate is more strongly adsorbed from aq. soln. than is the case with sodium succinate. According to N. N. Mittra and N. R. Dhar, the induced reactions involving the oxidation in air of cobalt hydroxide as primary reaction may have the oxidation of nickel hydroxide as a secondary reaction; and the oxidation of sodium sulphite as primary reaction with the oxidation of cobaltous hydroxides as secondary reaction. R. H. Brett found the hydroxide to be insoluble in a soln. of potassium



hydroxide; but E. Donath said that it forms a blue soln. with hot soln. containing over 30 per cent. of potassium or sodium hydroxide—*vide supra*. A. de Schulten found that when the hot soln. in alkali hydroxide is cooled, microscopic crystals of cobaltous hydroxide separate out on cooling. The hydroxide is soluble in a conc. soln. of potassium carbonate. A. Hantzsch observed that the rose-red hydroxide reacts with acetyl chloride and with benzoyl chloride more vigorously than is the case with the blue hydroxide. A. Bernardi and G. Piacentini observed that the hydroxide forms compounds with nitrophenols. F. Feigl studied the autoxidation of the rose-red hydroxide, and observed that it has the power of colouring benzidine blue, and the reaction has been used as a test for cobalt; toluidine behaves like benzidine. G. Natta and L. Passerini observed that cobaltous hydroxide forms a complete series of solid soln. with magnesium and manganous hydroxides, and a partial series of solid soln. with zinc hydroxide. O. Hahn and O. Müller studied the adsorption of radiothorium by the hydroxide.

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## § 11. Cobaltous Oxide and Intermediate Oxides

H. Moissan<sup>1</sup> said that cobaltous oxide is formed by allowing pyrophoric cobalt to burn in air. P. Sabatier and J. B. Senderens obtained this oxide by heating cobalt in air—S. Burgstaller said at 300° to 431°, and E. Donath observed that only the surface of the compact metal is so oxidized. F. Emich obtained this oxide by heating the metal in nitric oxide, but P. Sabatier and J. B. Senderens obtained cobaltous oxide in this way. W. Beetz, T. Carnelley and J. Walker, H. Hess, G. F. Hüttig and R. Kassler, F. Merck and E. Wedekind, C. F. Rammelsberg, G. C. Winkelblech, and J. L. C. Zimmermann obtained **cobaltous oxide**, Co<sub>3</sub>O<sub>4</sub>, by heating cobaltic oxide or hydroxide in air; and H. Moissan, by heating any of the

oxides of cobalt to 1000°. C. F. Rammelsberg found that the same oxide is formed when cobaltous oxide, hydroxide, carbonate, or oxalate, or, according to H. Rose, the basic carbonate, or a hydrated cobaltous oxide is heated to redness in air or oxygen—at a higher temp. the oxide formed corresponds with  $\text{Co}_3\text{O}_4$ . The conversion of cobaltous oxide into cobaltous oxide by calcination in air was observed by W. A. Lampadius, W. G. Mixter, W. J. Russell, and J. L. C. Zimmermann; H. T. Kalmus recommended a temp. of 640°; H. Moissan, and J. Pionchon, 900° to 1000°—but, added P. Hausknecht, the conversion to cobaltous oxide is not complete; according to L. Wöhler and O. Balz, and M. le Blanc and J. E. Möbius, the conversion is complete at 100° to 400° in an atm. of oxygen; and J. Milbauer found that at 480°, and in oxygen at 12 atm. press., the cobaltous oxide contains traces of higher oxides. F. Emich obtained cobaltous oxide by heating cobaltous oxide in nitric oxide at 400°. F. Glaser, S. F. Hermsbädt, J. L. Proust, T. W. Richards and G. P. Baxter, and L. J. Thénard obtained cobaltous oxide by roasting cobaltous hydroxide; and C. F. Rammelsberg, H. Hess, W. Beetz, P. Hausknecht, and G. C. Winkelblech found that at too high a temp. some cobaltous oxide is present. J. L. C. Zimmermann obtained cobaltous oxide by calcining the precipitate obtained by the action of mercuric oxide on a soln. of a cobalt salt. C. D. Braun, C. F. Bucholz, S. Burgstaller, P. H. Emmett and J. F. Schultz, E. Frémy, V. M. Goldschmidt and co-workers, W. Hempel and H. Thiele, J. A. Hedvall, G. F. Hüttig and R. Kassler, R. Kassler, G. Natta and M. Strada, and H. Remmler obtained it by calcining cobalt nitrate, at temp. between 300° and 800°; and F. Merck and E. Wedekind used a molten mixture of potassium and sodium nitrates at 300°, and obtained crystals of the oxide; they found 350° to be too high a temp. A. Schwarzenberg, and J. L. C. Zimmermann obtained crystals of cobaltous oxide by heating a dry mixture of ammonium chloride and cobalt oxalate or chloride in air or oxygen, and extracting the product with hot, conc. hydrochloric acid. A. Gorgeu obtained cobaltous oxide in crystals by passing moist air into molten cobaltous chloride at a bright red-heat, for 5 or 6 hrs., and adding more cobalt chloride from time to time to make up for that lost by volatilization, etc. The cobaltous oxide is produced by moisture and oxidizing gases, and not by moist carbon dioxide, or by dry air. K. Jellinek and A. Rudat passed oxygen over cobaltous chloride at 550°; and T. Vorster, passed a mixture of ammonia and air over the heated chloride. Crystals of cobaltous oxide were also made by H. Hess, and S. Holgersson by heating the chloride with sodium carbonate; A. Schwarzenberg, with potassium chlorite, or manganese dioxide; S. Holgersson, and L. Thompson, with potassium chlorate; and P. Gucci, with potassium nitrate. W. Hempel and H. Thiele, and F. Strohmeier obtained cobaltous oxide by roasting the sulphide; C. F. Rammelsberg, W. L. Dudley, W. G. Mixter, W. J. Russell, H. W. Foote and E. K. Smith, H. Rose, J. A. Hedvall, and S. Holgersson, by heating the carbonate or basic carbonate; and C. F. Rammelsberg, R. Schneider, and H. Hess, by heating the oxalate in air or oxygen—G. Chaudron recommended a temp. of 600°. O. W. Gibbs and F. A. Genth obtained cobaltous oxide in octahedral crystals by calcining cobaltic aquopentamminochloride, and other complex amines were found by J. L. Bell, C. D. Braun, H. Copaux, N. W. Fischer, E. Frémy, S. M. Jørgensen, G. von Knorre, C. Krause, A. Laugier, J. von Liebig, G. A. Quesneville, J. B. Rogojsky, E. Saint-Evre, G. Schroeder, A. Schwarzenberg, and L. J. Thénard, similarly, to yield cobaltous oxide. G. Grube and O. Feucht noted that cobaltous oxide is formed during the anodic oxidation of cobalt in potash-lye at low potentials.

The products obtained by calcining the oxides and salts of cobalt in air, is a black, or steel-grey, powder. A. Schwarzenberg, O. W. Gibbs and F. A. Genth, and A. Gorgeu said that the crystals are octahedral, and A. Gorgeu added that the angles are very different from those of hausmannite, so that cobaltous and manganous oxides are not isomorphous; but G. Natta and M. Strada found that the crystals of cobaltous oxide, and of zinc cobaltite,  $\text{Zn}(\text{CoO}_2)_2$ , are isomorphous; and that the X-radiograms of cobaltous oxide correspond with a cubic lattice of

the spinel type, with 8 mols. per unit lattice, having the parameter  $a=8.05$  Å., and volume  $253.61 \times 10^{-24}$ . G. Natta and M. Schmid gave  $a=8.02$  Å.; S. Holgersson,  $a=8.11$  Å.; S. B. Hendricks and W. H. Albrecht,  $a=8.04$  Å.; and P. P. Ewald and C. Hermann,  $a=8.07$  Å. The observations of G. Natta and M. Strada on the X-ray spectral lines are shown in Fig. 71. J. A. Hedvall, and G. Lunde made observations on the subject. S. B. Hendricks and W. H. Albrecht observed that the X-radiograms of cobaltous oxide resemble those of magnetite, but the differences in the lattice dimensions indicate that the atoms are closer in cobaltous oxide, but the structure is the same in both cases, as well as in the case of cobaltous ferrite. The observations of S. Holgersson and A. Karlsson, and G. Natta and M. Strada on the isomorphism of cobaltous oxide with the spinels, are discussed in connection with the cobaltites. C. F. Rammelsberg obtained 5.833 to 6.296 for the sp. gr. G. Natta and co-workers calculated 6.21 from the space-lattice data; G. Natta and L. Passerini, 6.11; S. Holgersson, 6.005; and S. B. Hendricks and W. H. Albrecht, 6.17. H. H. Stephenson discussed the mol. vol.; and F. Fischer and co-workers, the thermoelectric power.

C. D. Braun found that the black oxide is hygroscopic, and C. F. Cross added that it is converted into the hemitrihydrate, when it is exposed to moist air. When heated to bright redness, A. Gorgeu said that cobaltous oxide is gradually converted into cobaltous oxide, and that the curve for the transformation is continuous, *i.e.* without breaks. When cobalt monoxide is heated in air to dull redness, it absorbs oxygen, but at a higher temp. the oxygen is again partially expelled. H. Moissan found that cobaltous oxide is completely transformed into cobaltous oxide at temp. exceeding  $1000^\circ$ ; and L. Wöhler and O. Balz found that in a current of carbon dioxide, cobaltous oxide begins to decompose at  $600^\circ$ . H. W. Foote and E. K. Smith gave for the dissociation press.,  $p$  mm., of cobaltous oxide:

	$800^\circ$	$850^\circ$	$900^\circ$	$910^\circ$	$950^\circ$	$970^\circ$
$p$ . . . . .	10	28	144	183	521	765 mm.

The dissociation press. of the oxygen,  $p$  atm., for the reversible reaction:  $\text{Co}_3\text{O}_4 \rightleftharpoons 3\text{CoO} + \frac{1}{2}\text{O}_2$ , was found by L. Wöhler and O. Balz to be  $p=4.16 \times 10^{-28}$  at  $450^\circ$ ; W. Biltz gave 0.045 at  $837^\circ$ , 0.32 at  $937^\circ$ ; 0.78 at  $977^\circ$ ; and 1.74 at  $1037^\circ$ ; and M. le Blanc and J. E. Möbius, 0.16 at  $880^\circ$ . J. A. Hedvall obtained  $952^\circ$  for the dissociation temp. of cobaltous oxide made from the nitrate at  $450^\circ$ ; and when prepared from the carbonate at  $450^\circ$ , the dissociation temp. is  $922^\circ$ . J. Hagenacker observed that the dissociation press. of cobaltous oxide at  $953^\circ$  is 547 mm., and at  $984^\circ$ , about 1045 mm. G. Kröger studied the thermal dissociation of the oxide. J. E. Möbius found that there is a state of equilibrium,  $\text{Co}_3\text{O}_4 \rightleftharpoons 3\text{CoO} + \frac{1}{2}\text{O}_2$ . S. Burgstaller found that from the dissociation temp. of cobaltic oxide,  $372^\circ$  to  $373^\circ$ , to a point between  $705.5^\circ$  and  $869^\circ$ , cobaltous oxide is stable, and above that temp., cobaltous oxide is stable. The exact transition points cannot be determined because, he said, regions of solid soln. of the one oxide in the other must be traversed. Cobaltous oxide is formed between  $300^\circ$  and  $431^\circ$ , and, at  $869^\circ$ , there is a region where there are solid soln. of cobaltous and cobaltous oxides. The existence of these regions of solid soln., and the slow speed of dissociation have misled many chemists into assumptions involving the existence of *zahlreiche unwahrscheinliche Kobaltoxyde*. L. Wöhler stated that changes in the dissociation press. of an oxide at a constant temp. are due to the formation of solid soln., and not, as supposed by A. J. Allmand, to changes in the sizes of the molecules. M. Watanabe gave for the dissociation press., 23 mm. at  $855^\circ$ ; 81 mm. at  $897^\circ$ ; 174 mm. at  $928^\circ$ ; and 438 mm. at  $960^\circ$ . Below  $928^\circ$ , the system is bivariant and the dissociation press. depends on the composition; the system then becomes univariant when two solid

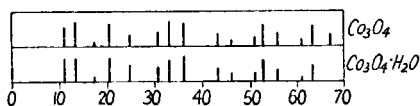


FIG. 71.—The X-ray Spectral Lines of Cobaltous Oxide and Hydroxide.

soln. of  $\text{CoO}$ , and  $\text{Co}_3\text{O}_4$  are formed. At  $960^\circ$  the system is bivariant. The thermal value of the reaction:  $\text{Co}_3\text{O}_4 \rightleftharpoons 3\text{CoO} + \frac{1}{2}\text{O}_2$ , is  $\delta Q = 38,972 - 0.75T + 0.00025T^2$ ; and the free energy,  $\delta F = 38,972 + 1.73T \log T - 0.00025T^2 - 36.07T$ ; and for the reaction:  $3\text{Co} + 2\text{O}_2 = \text{Co}_3\text{O}_4$ ,  $\delta Q = -206,074$  cal. at  $25^\circ$ , and  $\delta F = -181,355$  cal. at  $25^\circ$ .

J. E. Möbius, and M. le Blanc and J. E. Möbius noted that cobaltous oxide absorbs oxygen, forming the system  $\text{Co}_3\text{O}_4 \cdot n\text{O}_2$ , to such an extent that the analysis makes it appear as if an oxide higher than  $\text{Co}_2\text{O}_3$  were formed, although the lattice of  $\text{Co}_3\text{O}_4$  has undergone no change. Although the system  $\text{CoO} \cdot m\text{O}_2$  readily passes into  $\text{Co}_3\text{O}_4$ , the system  $\text{Co}_3\text{O}_4 \cdot n\text{O}_2$  shows no tendency to form the higher oxide  $\text{Co}_2\text{O}_3$ . Indeed, the so-called dry methods of preparing cobaltic oxide all yield a solid soln. of oxygen in cobaltous oxide. A. A. Read said that when cobaltous oxide is strongly heated in the oxyhydrogen flame, it yields metallic cobalt, and as the metal cools it becomes tarnished with a film of oxide. According to W. G. Mixter, the heat of formation of cobaltous oxide from its elements is  $(3\text{Co}, 2\text{O}_2) = 193.4$  Cals.; and from amorphous cobaltous oxide,  $(3\text{CoO}, \text{O}) = 41.9$  Cals. W. Biltz calculated values from observations on the dissociation press. M. le Blanc and H. Sachse gave  $10^{-4}$  mho for the electrical conductivity at  $18^\circ$ ; and K. Friederich gave 240,000 ohms per sq. mm. for the resistance. C. C. Bidwell found the thermo-electric force against lead, at different temp., furnishes a linear curve. A. Schwarzenberg said that, unlike ferrous oxide, cobaltous oxide is non-magnetic. F. Merck and E. Wedekind gave  $32 \times 10^{-6}$  mass unit for the magnetic susceptibility; P. Hausknecht gave  $34.4 \times 10^{-6}$  mass unit; and E. F. Herroun and E. Wilson,  $39.6 \times 10^{-6}$  to  $43.6 \times 10^{-6}$  mass unit. S. Meyer, and R. H. Weber measured the vol. susceptibility.

When cobaltous oxide is heated in **hydrogen**, it is reduced first to cobaltous oxide (*q.v.*), and then to the metal; W. Müller said that the reduction begins at about  $200^\circ$ ; F. Glaser, at about  $207^\circ$ ; and L. Wöhler and O. Balz, at  $350^\circ$ . G. Gallo said that the reduction of cobaltous oxide by hydrogen begins at about  $90^\circ$ —*vide infra*, cobaltic oxide. L. Wöhler and O. Balz found that the equilibrium constant of the reaction:  $\text{Co}_3\text{O}_4 + \text{H}_2 \rightleftharpoons 3\text{CoO} + \text{H}_2\text{O}$ , is  $34.4$  at  $450^\circ$ , whilst that for  $\text{CoO} + \text{H}_2 \rightleftharpoons \text{Co} + \text{H}_2\text{O}$ , is  $13.5$  at the same temp. B. Neumann and co-workers discussed the catalytic effect of the oxide on the oxidation of carbon monoxide.

I. L. Bell found that in the presence of water, cobaltous oxide is attacked by **iodine**. G. Gore observed no action by liquid **hydrogen fluoride** at  $-6.6^\circ$ . C. D. Braun, C. F. Bucholz, F. Emich, O. W. Gibbs and F. A. Genth, A. Laugier, F. Merck and E. Wedekind, J. L. Proust, J. B. Richter, E. Saint-Evre, and A. Schwarzenberg observed that **hydrochloric acid** slowly dissolves cobaltous oxide, with the evolution of chlorine; the solution is at first green, then blue, and in air it becomes violet, and, on the addition of water, red. O. Brunck observed that when heated with **potassium chlorate**, ozonized oxygen is evolved at  $250^\circ$ , and vigorously at  $300^\circ$ . M. le Blanc and J. E. Möbius found that a hydrochloric acid soln. of **potassium iodide** dissolves cobaltous oxide at  $60^\circ$ .

T. Hiortdahl observed that **hydrogen sulphide** at a red-heat converts cobaltous oxide into the sulphide  $\text{Co}_2\text{S}_3$ ; and F. Bourion, and C. Matignon and F. Bourion, that **sulphur monochloride** attacks cobaltous oxide below the b.p. of sulphur, forming sulphur, sulphur dioxide, and cobaltous chloride. O. W. Gibbs and F. A. Genth, J. L. Proust, and A. Schwarzenberg found that cobaltous oxide dissolves only slowly in **sulphuric acid**, and on heating the mixture, oxygen is evolved.

U. Sborgi and E. Gagliardo found that **boron nitride** at  $750^\circ$  to  $900^\circ$  decomposes cobaltous oxide with the formation of nitric oxide, and boric oxide, and when heated in air, cobaltous oxide is re-formed. C. Winkler observed that **ammonia** gas reduces the heated oxide; and E. Divers observed that the oxide is soluble in an ammoniacal soln. of **ammonium nitrate**; with molten **ammonium thiocyanate**, C. D. Braun obtained a blue mass. W. Beetz, C. F. Bucholz, O. W. Gibbs and

F. A. Genth, J. L. Proust, and A. Schwarzenberg found that **nitric acid** dissolves the oxide slowly, but not completely, and oxygen is evolved.

As indicated in connection with cobalt, **carbon** reduces the oxide to the metal; and likewise also **carbon monoxide**. E. Frémy observed that **acetic acid** forms a green to brown soln. G. C. Winkelblech, and E. Saint-Evre noted that with **oxalic acid**, carbon dioxide is evolved, and M. le Blanc and J. E. Möbius found that the reaction:  $\text{Co}_3\text{O}_4 + \text{H}_2\text{C}_2\text{O}_4 = 3\text{CoO} + 2\text{CO}_2 + \text{H}_2\text{O}$ , is quantitative. According to J. E. Möbius, cobaltous oxide dissolves in oxalic acid, forming a cobaltous salt, and absorbed oxygen oxidizes the acid very slowly, whilst the excess oxygen above cobaltous oxide oxidizes the oxalic acid very quickly. The results show that the product  $\text{Co}_3\text{O}_4 \cdot n\text{O}_2$ , or  $\text{CoO} \cdot m\text{O}_2$ , is not cobaltic oxide. A. Kutzelnigg studied the adsorption of **potassium ferrocyanide** by the oxide. T. M. Felton observed a eutectic with **silica** at  $1325^\circ$ , and 68 per cent.  $\text{Co}_3\text{O}_4$ .

J. L. Gay Lussac and L. J. Thénard found that molten **sodium** or **potassium** reduces the oxide to the metal; and, as indicated in connection with the preparation of the metal, **aluminium** also reduces the oxide to metal. According to A. Schwarzenberg, molten **sodium hydroxide** dissolves cobaltous oxide, forming a blue mass. J. A. Hedvall and N. von Zweigbergk studied the action of **barium peroxide**. H. Hess said that with molten **potassium hydroxide**, a brown mass is formed; J. L. Proust, that alkali-lye in the presence of tin, forms a red liquid; and C. Winkler, and E. Donath, that the boiling lye forms a blue soln. T. M. Felton studied the reaction with **alumina**; and S. Roginsky and E. Schultz, the catalytic action of the oxide on the thermal decomposition of **potassium permanganate**, and of **ammonium dichromate**. O. W. Gibbs and F. A. Genth observed that molten **potassium sulphate** dissolves cobaltous oxide.

C. D. Braun found if basic cobalt carbonate,  $3\text{CoO} \cdot 2\text{CO}_2 \cdot 4\text{H}_2\text{O}$ , be heated to  $200^\circ$ , the black residue corresponds with the *dihydrate*,  $\text{Co}_3\text{O}_4 \cdot 2\text{H}_2\text{O}$ . He also obtained a hydrate by heating cobaltous ferricyanide with alkali-lye; and G. Natta and M. Strada, by treating a soln. of cobaltous sulphate with alkali-lye and bromine, and drying the precipitate at a high temp. in air. H. Rose obtained what appeared to be  $4\text{Co}_3\text{O}_4 \cdot 3\text{H}_2\text{O}$ , by treating the basic carbonate,  $5\text{CoO} \cdot 2\text{CO}_2 \cdot 4\text{H}_2\text{O}$ , in a similar manner. E. Frémy, and C. F. Cross, as indicated previously, said that when the anhydrous oxide is exposed to a moist atmosphere, the composition of the product approaches  $2\text{Co}_3\text{O}_4 \cdot 3\text{H}_2\text{O}$ . G. Natta and M. Strada's observations on the X-ray spectral lines are indicated in Fig. 71. According to O. W. Gibbs and F. A. Genth, when a soln. of cobaltic aquopentamminsulphate is boiled, the *trihydrate*,  $\text{Co}_3\text{O}_4 \cdot 3\text{H}_2\text{O}$ , is formed, and similar results were obtained by A. B. Lamb and J. W. Marden; whilst, according to F. Mawrow, the same product is obtained when cobaltous hydroxide is treated with potassium persulphate, in neutral soln., and the black product boiled with dil. nitric acid (1:4). According to W. N. Hartley, the *hexahydrate*,  $\text{Co}_3\text{O}_4 \cdot 6\text{H}_2\text{O}$ , is formed when a cold soln. of cobaltous chloride is decomposed by boiling in vacuo with an eq. quantity of barium hydroxide. When the green product is treated with acetic acid, cobaltous oxide separates. E. Frémy prepared the *heptahydrate*,  $\text{Co}_3\text{O}_4 \cdot 7\text{H}_2\text{O}$ , by treating a soln. of cobalt salt with an excess of potassium hydroxide, and allowing the mixture to stand for a month in a flask containing oxygen. The brown product contaminated with some potassium salt, is dried in vacuo.

G. Natta and M. Strada said that the crystal lattice of the hydrated cobaltous oxide is the same as that of cobaltous oxide. C. D. Braun observed that the hydrate can be dehydrated only with difficulty; traces of water are retained at  $200^\circ$ ; cobaltous oxide is formed at bright redness, and, on cooling, a layer of cobaltous oxide is formed. According to O. W. Gibbs and F. A. Genth, the hydrated oxide is a dark brown powder, soluble in oxalic acid to form a green soln. which decomposes when heated. C. D. Braun, O. W. Gibbs and F. A. Genth, and F. Mawrow observed that hydrochloric acid dissolves it to form cobaltous chloride with the evolution of chlorine; the hydrated oxide is also soluble in dil. nitric



acid with a protracted boiling, but the conc. acid readily dissolves the hydrate. A. H. McConnell and E. S. Hanes observed that cobalt acetate is formed when the hydrate is treated with acetic acid, and E. Frémy thought that when hydrated cobaltous oxide is treated with acetic or sulphuric acid, cobaltous salts are formed.

**Oxides between  $\text{CoO}$  and  $\text{Co}_3\text{O}_4$ .**—As indicated above, S. Burgstaller<sup>2</sup> observed no evidence of the formation of intermediate oxides between  $\text{CoO}$  and  $\text{Co}_3\text{O}_4$ . There is a region of solid soln. of the two oxides in the vicinity of  $869^\circ$ . The existence of these solid soln., and the fact that the speed of transformation from one oxide to the other may be very slow, explains why numerous workers have obtained intermediate oxides. Again, J. E. Möbius, and M. le Blanc and J. E. Möbius observed that cobalt oxide readily forms solid soln. with oxygen  $\text{CoO} \cdot m\text{O}_2$  where the oxygen is not a part of the lattice structure. This unstable system when annealed may form  $\text{Co}_3\text{O}_4 \cdot n\text{O}_2$ . The absorbed oxygen in cobaltous oxide attacks oxalic acid slowly, whereas if the excess oxygen were present as a higher oxide the attack would be rapid.

C. R. A. Wright and A. P. Luff reported an oxide  $\text{Co}_{16}\text{O}_{17}$ . G. C. Winkelblech, H. Rose, and W. Beetz reported  $\text{Co}_6\text{O}_7$  to be formed by heating cobaltous hydroxide in air; W. Beetz, by heating cobaltous chloride or carbonate in air; and H. Rose, and J. M. Krok, by heating the basic carbonate in air. Observations on the  $\text{Co}_6\text{O}_7$ -oxide were made by C. D. Braun, O. W. Gibbs and F. A. Genth, H. Hess, S. M. Jörgensen, H. T. Kalmus, C. F. Rammelsberg, W. J. Russell, A. Sieverts, E. von Sommaruga, and A. Weissenborn. C. D. Braun, and H. Rose reported  $\text{Co}_4\text{O}_5$  to be formed by heating the basic carbonate in air at  $100^\circ$ , and P. Sabatier and J. B. Senderens, by burning reduced cobalt in nitrous oxide. Observations were also made by G. Gallo, E. Hüttner, A. Sieverts, and A. Weissenborn.

L. V. Brugnatelli, and J. G. Gentile reported  $\text{Co}_8\text{O}_9$  to be formed as an *octohydrate*,  $\text{Co}_8\text{O}_9 \cdot 8\text{H}_2\text{O}$ , when the freshly-precipitated cobaltous hydroxide is heated with soln. of potassium hydroxide until it forms a dark brown product. W. N. Hartley obtained a buff-coloured *henahydrate*,  $\text{Co}_8\text{O}_9 \cdot 11\text{H}_2\text{O}$ , by the action of an excess of barium hydroxide on a boiling soln. of cobalt nitrate in vacuo. G. C. Winkelblech, C. D. Braun, and J. G. Gentile obtained the *icosihydrate*,  $\text{Co}_8\text{O}_9 \cdot 20\text{H}_2\text{O}$ , by exposing the blue ammonia precipitate of cobaltous hydroxide to air until it becomes yellow, or by adding potassium hydroxide to a mixture of cobalt sulphate and ammonia, and warming the green precipitate at  $30^\circ$  until it becomes yellow. E. J. Mills reported the hydrated oxide,  $\text{Co}_4\text{O}_5 \cdot n\text{H}_2\text{O}$ , to be formed by heating cobaltic hexamminochloride with 30 to 40 times its weight of water in a sealed tube at  $70^\circ$  to  $100^\circ$ .

Between  $372^\circ$ , the dissociation temp. of cobaltic oxide, and a temp. between  $705.5^\circ$  and  $869^\circ$ , cobaltous oxide is stable. The transformation temp. are difficult to determine because of the formation of solid soln. of one oxide in the other. J. E. Möbius, and M. le Blanc and J. E. Möbius observed that cobaltous oxide can form a solid soln. with oxygen,  $\text{Co}_3\text{O}_4 \cdot n\text{O}_2$ , even to the case where the cobaltous oxide dissolves more oxygen than corresponds with cobaltic oxide, without forming that oxide. Indeed, J. E. Möbius said that all the described processes for preparing cobaltic oxide really furnish solid soln. of  $\text{Co}_3\text{O}_4 \cdot n\text{O}_2$ . When the solid soln. is treated with oxalic acid, the excess of oxygen corresponding with cobaltous oxide rapidly oxidizes the acid whilst the free oxygen reacts only slowly, thus showing that the solid soln. is cobaltous and not cobaltic oxide. G. Natta and M. Strada could not prepare oxides or hydroxides of cobalt between  $\text{Co}_2\text{O}_3$  and  $\text{Co}_3\text{O}_4$  as chemical individuals. The X-radiograms showed that the products were all mixtures.

E. J. Mills reported the  $\text{Co}_6\text{O}_7$ -oxide, and also  $\text{Co}_7\text{O}_{10}$ , formed by heating cobaltic hexamminochloride or chloropentamminodichloride with 2 mols. of cobalt chloride and water in a sealed tube at  $100^\circ$ ; and R. L. Taylor, by treating a neutral soln. of cobalt chloride with bromine and an alkaline earth carbonate, obtained oxides ranging from  $\text{Co}_7\text{O}_{11}$  to  $\text{Co}_9\text{O}_{14}$ . T. Bayley reported  $\text{Co}_{12}\text{O}_{19}$ -oxide; and T. Bayley, G. Schroeder, and G. Rousseau, the  $\text{Co}_2\text{O}_5$ -oxide. N. McCulloch reported an oxide,  $\text{Co}_{13}\text{O}_{19}$ , to be formed by the action of hydrogen dioxide, in the presence of free alkali, on a boiling soln. of a cobalt salt. C. R. A. Wright and A. P. Luff, and N. McCulloch reported the hydrate,  $\text{C}_{13}\text{O}_{19} \cdot n\text{H}_2\text{O}$ , to be formed by boiling a cobaltous salt with an excess of potash-lye and bromine, or with a strongly-alkaline soln. of hydrogen dioxide. R. L. Taylor likewise

obtained  $\text{Co}_2\text{H}_{14}\cdot n\text{H}_2\text{O}$ ; C. R. A. Wright and A. P. Luff, T. Bayley, E. Hüttner, R. Fischer, and G. Schroeder,  $\text{Co}_{11}\text{O}_{11}\cdot n\text{H}_2\text{O}$ ; A. Carnot, E. Hüttner, A. B. Lamb and co-workers, and G. Schroeder,  $\text{Co}_5\text{O}_8\cdot n\text{H}_2\text{O}$ ; T. Bayley, K. A. Hofmann and H. Hiendlmaier, G. Natta and M. Strada, G. Schroeder, and G. C. Winkelblech,  $\text{Co}_3\text{O}_5\cdot n\text{H}_2\text{O}$ ; and J. Thomsen,  $\text{Co}_4\text{O}_7\cdot 7\text{H}_2\text{O}$ .

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### § 12. Cobaltic Oxide and its Hydrates

L. V. Brugnatelli noted the formation of a salt of a higher cobalt oxide when the yellow soln. of cobaltous hydroxide in aq. ammonia is exposed to air. The liquid becomes red. The product was studied by J. B. Trommsdorff.<sup>1</sup> J. L. Proust thought that **cobaltic oxide**, Co<sub>2</sub>O<sub>3</sub>, is formed when cobaltous nitrate is calcined at a low enough temp. in air; and G. C. Winkelblech added that to expel all the nitric acid, the product, calcined at about 184°, should be finely ground, and gently heated in a porcelain crucible until red vapours are no longer evolved. H. Hess recommended decomposing cobaltous chloride in the dry way with sodium carbonate, and washing the residue with water. If the cobaltic oxide be prepared at too high a temp., it passes into cobaltous oxide. According to L. Thompson, the oxide is formed when a conc. soln. of cobaltous chloride, mixed with 1 to 1.5 parts of potassium chlorate, is evaporated to dryness, heated to dull redness and then extracted with water.

The brown, or brownish-black powder, according to the analyses of G. C. Winkelblech, J. L. Proust, E. Rothoff, and W. Beetz, corresponds with Co<sub>2</sub>O<sub>3</sub>, but J. E. Möbius, and M. le Blanc and J. E. Möbius doubt very much if cobaltic oxide can be produced in the dry way, although the hydrated oxide can be readily prepared. The alleged cobaltic oxide is considered to be a solid soln. of oxygen in cobaltous oxide—*vide supra*. N. A. Held observed that cobaltic oxide forms a **colloidal solution** in alcohol, when hydrochloric acid is used as peptizing agent.

G. Natta and M. Strada examined the X-radiograms of what they considered to be cobaltic oxide and its hydrates, Fig. 72; and they concluded that cobaltic oxide has probably a hexagonal or rhombohedral structure with a cell having the edge  $a=4.64$  Å., and  $c=5.75$  Å., so that  $a:c=1:1.24$ . There are two molecules per unit cell. G. Lunde, and V. M. Goldschmidt and co-workers found that the X-radiograms of cobaltic oxide corresponded with those of cobaltous oxide, and said that it is doubtful if cobaltic oxide has been prepared. The X-ray spectrum of cobaltous oxide (Fig. 71), however, differs from that of cobaltic oxide. The calculated sp. gr. is 5.34; W. Herapath reported 5.322 at  $16.5^\circ$ ; P. F. G. Boullay, 5.600; and L. Playfair and J. P. Joule, 4.814. H. Hess, and G. C. Winkelblech observed that

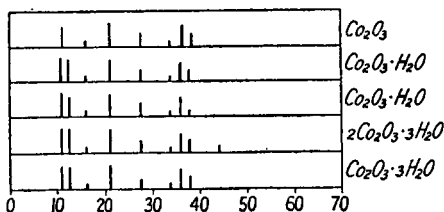


FIG. 72.—X-ray Spectra of Cobaltic Oxide and its Hydrates.

cobaltic oxide passes into cobaltous oxide when heated to dull redness, and J. L. Proust observed that at a higher temp., cobaltous oxide is formed. S. Burgstaller found that the dissociation temp. of cobaltic oxide is  $372^\circ$  to  $373^\circ$  at 760 mm. From this temp. up to  $705.5^\circ$  to  $869^\circ$ , cobaltous oxide is the stable form, and beyond that, cobaltous oxide. As indicated above, G. Natta and M. Strada said that cobaltic oxide forms cobaltous oxide at  $265^\circ$ . According to V. M. Goldschmidt and co-workers, G. Lunde, M. le Blanc and J. E. Möbius, and S. Holgersson, the oxide formerly considered to be cobaltic oxide, obtained by calcining cobaltous compounds in air, or treating them with oxidizing agents, is really cobaltous oxide,  $\text{Co}_3\text{O}_4$ . G. F. Hüttig and R. Kassler said that the product obtained by dehydrating hydrated cobaltic oxide is also cobaltous oxide, but G. Natta and M. Strada prepared cobaltic oxide by heating one of the hydrated forms, and added that no known process of preparation furnishes cobaltic oxide if the temp. employed exceeds  $250^\circ$ ; since at temp. above  $265^\circ$ , the product is cobaltous oxide. W. W. Coblenz studied the reflecting power of the oxide; and A. H. Barnes, the X-ray spectrum. K. Friederich gave 194,000 ohms per sq. mm. for the electrical resistance; and H. Reynolds found for the resistance,  $R$ , of pencils made by compressing powdered cobaltic oxide:

	$18^\circ$	$268^\circ$	$349^\circ$	$464^\circ$	$600^\circ$	$770^\circ$
$R$ . . .	22,800	1410	712	249	107	26.4 ohms

and the electrical conductivity of another sample exhibited a transformation in the vicinity of  $900^\circ$ , Fig. 73. This was thought to be due to the change of cobaltic into cobaltous oxide—from the above, it is more likely to have been  $\text{Co}_3\text{O}_4 \rightarrow \text{CoO}$ . The conductivities of mixtures of ferric and cobaltic oxides were also measured.

According to W. Müller, hydrogen reduces cobaltic oxide at  $125^\circ$  to cobaltous oxide, whilst cobaltous oxide is reduced at  $320^\circ$ ; H. Moissan said that cobaltic oxide is reduced to cobaltous oxide at  $190^\circ$  to  $200^\circ$ , and at  $250^\circ$ , to cobalt; S. Hauser said that hydrogen begins to reduce cobaltic oxide at  $225^\circ$  to  $240^\circ$ ; C. R. A. Wright and A. P. Luff, at  $110^\circ$ ; and F. Gläser, at  $182^\circ$ . G. Gallo said that there is an incipient reduction of cobaltic oxide by hydrogen at  $80^\circ$  to  $85^\circ$ ; and at a higher temp. there is a transient formation of cobaltous oxide which begins to be reduced to cobaltous oxide at about  $90^\circ$ . In the presence of water vapour, at 70 mm. press., the reduction of cobaltic oxide by hydrogen begins at  $95^\circ$ , and at  $110^\circ$  if the vap. press. of water is

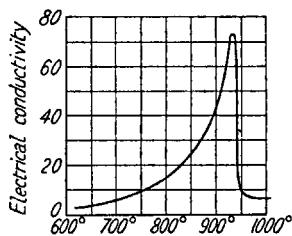


FIG. 73.—Electrical Conductivity of Cobaltic Oxide at Different Temperatures.

92 mm. O. Brunck found that when cobaltic oxide is heated in oxygen to  $400^{\circ}$ , or the beginning of a red-heat, some ozone is formed. In the dry state, cobaltic oxide cannot be oxidized to cobalt dioxide. According to C. F. Cross, when cobaltic oxide is exposed to a moist atmosphere, it gradually forms  $\text{Co}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ , or  $2\text{Co}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ , and then  $\text{Co}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ; the subject was discussed by W. Müller-Erzbach. Cobaltic oxide is decomposed by most acids in the cold with the formation of cobaltous salts. Chlorine is evolved when the oxide is digested with hydrochloric acid, and the reaction was studied by R. Finkener. A. Coehn and M. Gläser said that in consequence of the development of chlorine when cobaltic oxide is treated with hydrochloric acid, this oxide behaves more like lead and manganese dioxides than does ferric oxide—assuming, of course, that cobaltic oxide is a true sesquioxide like ferric oxide. G. J. Fowler and J. Grant observed that when heated with potassium chlorate, at about  $250^{\circ}$ , the oxygen which is evolved is accompanied by some chlorine. A. F. Benton studied the adsorption of oxygen, and carbon monoxide, and dioxide by cobaltic oxide at  $0^{\circ}$  and at  $-79^{\circ}$ . When heated with sulphur and water, J. B. Senderens observed that cobalt sulphate and thiosulphate are formed. C. Dufraisse and D. Nakae studied the catalytic oxidation of soln. of sodium sulphite. T. Vorster observed that when cobaltic oxide is heated in dry ammonia, cobaltous oxide is formed, and afterwards cobalt. F. Neumann, and O. Brunck examined the action of cobaltic oxide on carbon; and K. Iwase and M. Fukushima observed that the reduction is favoured by the presence of lime. C. R. A. Wright and A. P. Luff observed that carbon begins to reduce cobaltic oxide at  $260^{\circ}$ , and carbon monoxide at  $-11^{\circ}$ . F. Bullheimer observed that glycerol does not reduce cobaltic oxide. A. Bonnet said that cobaltic oxide is taken up from ammoniacal soln. by plant fibres. Cobaltic oxide dissolves in acetic acid without immediate decomposition. G. Rauter observed that silicon tetrachloride is decomposed by this oxide, forming silica, chlorine, and cobaltous chloride. C. Dufraisse and D. Nakae studied the catalytic oxidation of acetaldehyde, phenylaldehyde, furfuraldehyde, styrene, and turpentine. S. B. Hendricks and W. H. Albrecht prepared what may be **cobaltic ferrite**,  $\text{Co}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ —*vide* the ferrites.

**Hydrated cobaltic oxides.**—A number of impure forms of hydrated cobaltic oxide has been reported to occur in nature; the mineral **transvaalite**, described by T. B. McGhie and J. Clark, is an oxidation product of cobalt arsenide, and it occurs in black, nodular masses in veins in the quartzite near Middleburg, Transvaal. It is an impure **hydrated cobaltic ferric oxide**. It dissolves in hydrochloric acid with the liberation of chlorine. Its sp. gr. is 3.846, and its hardness, 4.0.

The mineral **heterogenite**, described by A. Frenzel, occurs in the veins of cobalt and nickel ores at Schneeberg, and at Heubach near Wittichen, Baden. It is a decomposition product of smaltite. It is amorphous, and occurs in black or reddish-brown, globular or reniform masses with little lustre. Its composition approximates the **hydrated cobaltic oxide**,  $\text{CoO} \cdot 2\text{Co}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ . Its sp. gr. is 3.44, and its hardness, 3. J. Morozewicz described **lubeckite**,  $\text{CuO} \cdot m(\text{Mn}, \text{Co})_2\text{O}_3 \cdot n\text{H}_2\text{O}$ , a black, colloidal mineral occurring at Miedzianka; the sp. gr. is 4.8, and the hardness, 2 to 3.

The black mineral **heubachite** occurs in thin, soot-like incrustations, or in dendritic or small spherical aggregates, as a secondary product in mines near Heubachtal, Baden; near Alpirsbach, Württemberg; and in Copiapo, Chili. It was described by F. Sandberger, who showed that it is a **hydrated cobaltic nickelic ferric oxide**,  $3(\text{Fe}, \text{Co}, \text{Ni})_2\text{O}_3 \cdot 4\text{H}_2\text{O}$ . Its sp. gr. is 3.75, and its hardness, 2.5. It is soluble in conc. hydrochloric acid with the evolution of chlorine; the soln. is bluish-green, and it becomes rose-red when diluted with water.

A. Schoep and V. Cuvelier, and V. Cuvelier described a mineral from Mindingi, Katanga, Belgian Congo. The analysis approximates **hydrated aluminium cobaltic oxide**,  $(\text{Fe}, \text{Al}, \text{Co})_2\text{O}_3 \cdot \text{H}_2\text{O}$ . It was called **stainierite**. It is black, compact, and opaque, with a granular or banded, concentric texture. It is birefringent and pleochroic. Its sp. gr. is 4.137, and its hardness, 4.5. It readily dissolves in hydrochloric acid with the evolution of chlorine. It is possibly isomorphous with goethite.

The oxidation of cobaltous salts in acidic or alkaline soln. furnishes hydrated cobaltic oxide. The composition of the hydrate depends on the concentration of the soln., the temp., the oxidizing agent, etc. Quite a number have reported

the formation of the hydrated oxide without specifying clearly the composition of the product, presumably because that was a secondary consideration to the main purpose of the work. The brown product obtained when precipitated cobaltous hydroxide is exposed to air, was shown by G. F. Hüttig and R. Kassler, and A. Remelé to contain cobaltous hydroxide, and does not consist wholly of cobaltic hydroxide. Various oxidizing agents have been recommended for converting hydrated cobaltous oxide into hydrated cobaltic oxide :

A. Carnot, R. G. Durrant, R. Fischer, G. F. Hüttig and R. Kassler, C. Krause, A. H. McConnell and E. S. Hanes, N. McCulloch, C. Paal and H. Boeters, A. Sieverts, and S. Veil oxidized soln. of cobalt salts with hydrogen dioxide ; O. Brunck, S. W. Parr, S. R. Benedict, and G. Natta and M. Strada, with sodium dioxide ; C. Reichard, with barium dioxide ; O. W. Gibbs, F. Gauhe, C. Krause, and H. Rose, with lead dioxide ; W. Beetz, P. Berthier, C. D. Braun, T. Carnelley and J. Walker, C. F. Cross, E. Frémy, P. Hausknecht, E. Hüttner, W. A. Lampadius, A. H. McConnell and E. S. Hanes, T. Moore, J. L. Proust, A. Quartaroli, C. F. Rammelsberg, H. Rose, C. L. Taylor, J. Thomsen, T. Vorster, and G. C. Winkelblech, with chlorine in alkaline soln. ; G. C. Winkelblech, W. Beetz, C. D. Braun, H. Rose, A. Weissenborn, A. F. Benton, E. Donath, F. Meidert, H. Hess, W. Müller, E. Fleischer, E. and B. Klimenko, S. Veil, and J. Thomsen, with sodium hypochlorite. According to G. C. Winkelblech, if alkali be not added to the soln. of cobalt nitrate after the addition of sodium hypochlorite, the cobalt forms soluble cobaltic nitrate. E. M. Dingler thought it was present in soln. as sodium cobaltite. H. Hess, and R. Böttger oxidized the cobalt salt with bleaching powder ; G. Natta and M. Strada, with potassium chlorate at 150° ; G. Natta and M. Strada, H. Remmler, E. Donath, C. Krause, A. Jorissen, E. Fleischer, G. F. Hüttig and R. Kassler, R. Kassler, F. Merck and E. Wedekind, A. J. Balard, T. Moore, and G. Schröder, with bromine ; E. Hüttner, and E. Donath, with iodine ; S. E. Moody, with iodates ; E. Hüttner, L. Dede, and F. Mawrow, with ammonium or potassium persulphate ; D. Bhaduri and P. Ray, with potassium ferricyanide ; F. Gauhe, T. W. Richards and G. P. Baxter, C. Krause, and C. Winkler, with potassium permanganate ; S. Kitashima, sodium bismuthate ; and N. W. Fischer, W. Wernicke, A. Coehn and Y. Osaka, A. Coehn and M. Gläser, F. Förster and E. Müller, F. Förster and A. Piguet, H. G. Byers, R. Saxon, E. Müller and F. Spitzer, E. Hüttner, C. Thieme-Wiedtmarckter, G. Grube and O. Feucht, G. Grube, and F. W. Skirrow, by anodic oxidation.

M. le Blanc and J. E. Möbius obtained hydrated cobaltic oxide by adding potash-lye to a soln. of anodically oxidized cobalt sulphate in 8N-H<sub>2</sub>SO<sub>4</sub> ; C. D. Braun, A. Carnot, E. Frémy, J. G. Gentile, O. W. Gibbs and F. A. Genth, L. Gmelin, C. Künzel, E. J. Mills, J. B. Rogojsky, and G. C. Winkelblech, by boiling aq. soln. of cobaltic amines, or by treating them with alkali-lye. Other complex cobaltic salts have been employed by S. R. Benedict, H. Colin and A. Sénéchal, E. Fleischer, C. Friedheim and F. Keller, R. Kassler, C. Krause, H. Rose, E. Saint-Evre, A. Stromeyer, and G. F. Hüttig and R. Kassler. G. F. Hüttig and R. Kassler recommended the following process :

Add a soln. of 18 grms. of potassium hydroxide in 50 grms. of water to a soln. of 10 grms. of cobaltic hexamminochloride (or chloropentamminochloride) in 300 grms. of water at 60° ; wash the precipitate by decantation with 5 litres of water, and filter by suction with the exclusion of air ; then wash it with another 5 litres of water ; and dry the product over sulphuric acid in vacuo.

According to W. Beetz, C. F. Bucholz, E. Donath, E. Donath and J. Mayrhofer, L. Gmelin, J. L. Proust, L. J. Thénard, O. Völker, and C. Winkler, cobaltous oxide dissolves in fused potassium hydroxide to form a clear, blue liquid, which with a more prolonged heating turns brown, and cobaltic oxide separates out in brown flakes. The blue liquid solidifies to a blue glass. The formation of the blue soln. by the action of alkali-lye on cobalt was discussed by C. D. Braun, E. Donath, G. Grube, G. Grube and O. Feucht, C. Tubandt, and C. Winkler. Again, J. L. Proust observed that when a soln. of a cobalt salt is dropped into boiling, conc. potash-lye, a blue precipitate is formed, that changes to a red hydrate, and afterwards dissolves to form a blue soln. When the blue soln. is sufficiently diluted with water, cobaltous hydroxide is deposited, but if air has access to the liquor, brown, hydrated cobaltic oxide is precipitated. Similar observations were made by O. Völker, and W. Beetz added that the soln. of cobaltous hydroxide in potassium

hydroxide is colourless if air be rigorously excluded; the blue coloration develops only when air has access to the liquor. C. Winkler showed that the blue soln. is developed when potassium hydroxide acts on reduced cobalt, or on cobaltous oxide, in air. The blue soln. gives reactions characteristic of cobaltic oxide, and he assumed that the blue colour is produced by a *Kobaltsäure*. W. Schulze, and E. Donath showed that a higher oxide is present when the blue colour is developed. The subject was studied by A. Remelé, G. C. Winkelblech, F. Reichel, E. Donath, G. Grube and O. Feucht, W. J. Russell, H. Ditz, and C. Tubandt. For C. W. Stillwell's observations, *vide supra*, cobaltous hydroxide.

G. Grube and O. Feucht observed that in conc. soln. of potassium hydroxide, anodic cobalt dissolves at high current-densities with the formation of a deep blue soln. of potassium cobaltite,  $\text{Co} + 2\oplus = \text{Co}^{++}$ ; and  $\text{Co}^{++} + 4\text{OH}' \rightleftharpoons \text{CoO}_2'' + 2\text{H}_2\text{O}$ ; or  $\text{Co}^{++} + 3\text{OH}' \rightleftharpoons \text{HCoO}_2' + \text{H}_2\text{O}$ . The electrode potentials of cobalt against blue soln. containing different amounts of cobalt in 8*N*-KOH, show that the blue soln. is potassium cobaltite, and not colloidal  $\text{Co}(\text{OH})_2$ , as suggested by C. Tubandt. The normal potential of cobalt against potassium cobaltite is -0.52 volt. The anodic oxidation of potassium cobaltite at a platinum anode takes place in 3 stages: (i) at low potentials, cobaltous oxide is formed; (ii) at medium potentials, cobaltic oxide is produced; and (iii) at high potentials, there results a solid soln. of cobalt dioxide in a lower oxide, and oxygen is evolved. The evolution of oxygen at a cobalt anode in alkali-lye involves the formation of cobalt dioxide and its subsequent decomposition into molecular oxygen and cobaltic oxide.

J. L. Proust, A. de Schullen, and C. Tubandt observed that the blue soln. is fairly stable in air, and deposits cobaltous hydroxide only slowly. It can be evaporated very far without decomposition, but when dried, C. Winkler observed the separation of a black oxide; and C. Winkler, and J. L. C. Zimmermann also noted that cobaltous hydroxide is deposited when the soln. is diluted. The soln. was found by C. D. Braun, E. Donath, E. Donath and J. Mayrhofer, J. L. Proust, and J. L. C. Zimmermann to be readily oxidized by air with the separation of cobaltic hydroxide. E. Donath, and C. Winkler also said that the soln. is readily oxidized to cobaltic hydroxide by hydrogen dioxide, and by chlorine. C. Winkler said that the soln. oxidizes potassium iodide, sulphur dioxide, potassium ferrocyanide and indigo, but E. Donath could not confirm this. C. Winkler found that with phosphorus, the blue soln. forms cobalt phosphide; and that carbon dioxide precipitates cobalt carbonate; E. Donath observed that ammonium sulphide precipitates cobalt sulphide; C. D. Braun, and E. Donath, that an excess of potassium cyanide forms potassium cobaltcyanide; C. Winkler, that zinc precipitates crystalline cobalt; and C. Tubandt, that barium sulphate precipitates cobaltous hydroxide.

When equal vols. of a soln. of sodium tartrate (50 per cent.), cobalt sulphate (30 per cent.), and sodium hydroxide (30 per cent.) are mixed, a violet-red soln. is obtained, and this on exposure to air develops a green colour which slowly becomes more intense. The green soln. was investigated by F. Field, F. Kehrmann, J. Gibson, H. Marshall, and R. G. Durrant. A. H. McConnell and E. S. Hanes showed that the soln. possibly contain percobaltites of the alkali metals in which  $\text{CoO}_2$  takes the place of  $\text{MnO}_2$  in the permanganites. A. Job found the at. ratio of Co : O in the green soln. is 2 : 3, *i.e.*  $2\text{CoO} + \text{O} = \text{Co}_2\text{O}_3$ . R. G. Durrant suggested that derivatives of cobaltic acid,  $\text{H}_2\text{CoO}_4$ , are present, since the green soln. is also produced by the action of hydrogen dioxide on soln. of cobalt salts in the presence of an excess of alkali hydrocarbonate. A. Job found that with the tartrate soln. just indicated, the amount of oxygen absorbed increases indefinitely under these conditions, but if a quantity of glycerol is added, it reaches a maximum, equivalent to one atom of oxygen for each atom of cobalt present. The cobaltic compound formed requires merely the absorption of an atom of oxygen for every two atoms of cobalt present, and it is suggested that the reaction which takes place may be represented by one of the two following sets of equations: (i)  $2\text{CoO} + \text{O}_2 = 2\text{CoO}_2$ , followed by  $2\text{CoO}_2 + \text{A} = \text{Co}_2\text{O}_3 + \text{AO}$ ; or else (ii)  $2\text{CoO} + \text{H}_2\text{O}$

$=\text{Co}_2\text{O}_3 + \text{H}_2$ , and  $\text{H}_2 + \text{O}_2 = \text{H}_2\text{O}_2$ , followed by  $\text{H}_2\text{O}_2 + \text{A} = \text{AO} + \text{H}_2\text{O}$ , where A denotes the acceptor which is an oxidizable compound—in the present case, tartaric acid. The second explanation was suggested by W. Manchot and co-workers; and the first explanation by A. Job, C. Engler, and E. Baur. In confirmation, A. Job found that manganous hydroxide, dissolved in an alkaline soln. of a tartrate, passes first into manganese dioxide and finally into the sesquioxide. Both cobaltous and manganous hydroxides under these conditions also absorb nitrosyl, but whereas the manganese soln. absorbs oxygen fifty times as quickly as the cobalt soln., the latter absorbs nitrosyl at least ten times as rapidly as the manganese solution.

**The preparation of definite hydrates of cobaltic oxide.**—A number of hydrated cobaltic oxides has been reported. Thus, E. J. Mills said that the *tritadihydrate*,  $3\text{Co}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ , is formed when a molar proportion of cobaltic chloropentamminodichloride and two molar proportions of cobaltous chloride are heated with water while exposed to the air. The *hemitrihydrate*,  $2\text{Co}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ , was reported by E. Hüttner to be formed by drying the tritapentahydrate over conc. sulphuric acid; by treating a soln. of cobalt sulphate with potassium hydroxide and oxidizing the product with potassium persulphate, or with chlorine. C. F. Cross also recommended chlorine for oxidizing cobaltous hydroxide suspended in potash-lye, and drying the product at  $100^\circ$  to a constant weight. G. F. Hüttig and R. Kassler showed that the dehydration curves indicate the existence of a *monohydrate*,  $\text{Co}_2\text{O}_3 \cdot \text{H}_2\text{O}$ —*vide infra*. According to F. Mawrow, if 4 grms. of cobaltous hydroxide be suspended in a soln. of 100 grms. of potassium hydroxide of sp. gr. 1.12, and warmed with an excess of potassium persulphate, there is formed a yellow precipitate which turns brown, and then black. It is washed with hot water, and dried over sulphuric acid. When this is treated with warm nitric acid, there remains a brownish-black mass which when dried approximates  $2\text{Co}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ —and it is said that the product is possibly a mixture of  $\text{Co}_2\text{O}_3$  and  $\text{Co}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ . E. Hüttner reported that the *tritapentahydrate*,  $3\text{Co}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ , is formed when a soln. of 10 grms. of cobaltous sulphate in a little water is treated with 200 c.c. of a sat. soln. of potassium persulphate; and also when an ammoniacal soln. of cobalt and ammonium sulphates is treated with potassium persulphate.

According to E. Hüttner, when the tritapentahydrate is exposed for 9 days over sulphuric acid, the product passes into the *dihydrate*,  $\text{Co}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ . H. Hess, and C. D. Braun also obtained the dihydrate by drying the trihydrate for a week over conc. sulphuric acid. E. Hüttner obtained the dihydrate by treating 10 grms. of cobalt sulphate with an excess of potash-lye, and a hot soln. of 20 grms. of potassium persulphate in 100 c.c. of water; or by treating a soln. of 5 grms. of cobalt sulphate in 150 c.c. of water with 100 c.c. of 20 per cent. potash-lye, and saturating the cold mixture with chlorine. A. Remelé obtained the dihydrate by adding potash-lye to an alcoholic soln. of cobaltous nitrate at  $60^\circ$  to  $80^\circ$ . W. Wernicke, and A. Coehn and M. Gläser also obtained the dihydrate by the electrolysis of a soln. of potassium cobalt tartrate in potash-lye, and drying the product in vacuo.

According to G. C. Winkelblech, and J. L. Proust, the *trihydrate*,  $\text{Co}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ , or **cobaltic hydroxide**,  $\text{Co}(\text{OH})_3$ , can be obtained by treating cobaltous hydroxide or carbonate suspended in water, with chlorine—C. D. Braun suspended the hydroxide in a boiling soln. of sodium hydroxide; H. Hess, and R. Böttger used bleaching powder as the oxidizing agent; G. C. Winkelblech, and G. Schröder, sodium hypochlorite; and A. J. Balard, bromine—R. Bernard and P. Job said that probably cobalt dioxide is formed as an intermediate product in the oxidation of cobaltous to cobaltic oxide. G. C. Winkelblech exposed a soln. of a cobaltous salt, saturated with ammonia, in air, until it formed a brown liquid, he then precipitated the product with potash-lye. E. Frémy boiled soln. of the cobalt amines with potash-lye. According to F. Mawrow, when a soln. of cobalt sulphate or nitrate is warmed with an excess of potassium persulphate, a dark brown precipitate, containing  $\text{Co}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  mixed with sulphates, is formed. The trihydrate is produced by warming cobaltous hydroxide with potassium persulphate, and, after



washing with water, heating the product at  $100^{\circ}$  with dil. nitric acid. About one-third of the cobaltous hydroxide is converted to hydrated cobaltic oxide. S. E. Moody treated a soln. of cobalt sulphate with potassium iodide and iodate. A. Coehn and M. Gläser obtained the trihydrate by the anodic oxidation of an alkaline soln. of cobalt tartrate. J. E. Root observed that with a soln. of 0.0870 gm. of cobalt in an alkaline soln. of tartrate, 0.0802 gm. of cobalt was deposited as metal on the cathode, and 0.0122 gm. of  $\text{Co}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  was deposited on the anode. C. F. Cross observed that when the hydrated oxide, which has been dried at  $100^{\circ}$ , is exposed to air saturated with moisture, for a few days, it forms either a *tetrahydrate* or a *pentahydrate*.

G. Schröder, G. F. Hüttig and R. Kassler, and F. Merck and, E. Wedekind observed that precipitated hydrated cobaltic oxide is readily peptized when it is washed with water. C. Paal and H. Boeters, and Kalle and Co. prepared **colloidal solutions** of cobaltic hydroxide with sodium protalbate or lysalbate as protective agent. During dialysis, the cobaltous hydroxide is oxidized to the cobaltic state. By evaporating the dialyzed soln., the product is soluble and the resulting colloidal soln. contains less than 10 per cent. of cobalt. If the colloidal cobaltic hydroxide be prepared in the presence of hydrogen dioxide, a stable, soluble colloid can be obtained with over 20 per cent. of cobalt. F. G. Tryhorn and G. Jessop obtained the colloid by adding ammonia to a mixture of hydrogen dioxide and cobalt chloride soln. The brown sol soon coagulated. L. Hugounenq and J. Loiseleur used glycogen as a protective colloid; and A. V. Dumansky and B. G. Zaprometoff, sodium tartrate and mannitol.

**The properties of hydrated cobaltic oxides.**—These hydrates are described by G. C. Winkelblech, and others as dark brown powders; and H. Herrenschildt and E. Capelle added that if pure, the colour is light brown. On the other hand, G. F. Hüttig and R. Kassler said that cobaltic hydroxide is black, and that brown preparations contain cobaltous hydroxide. G. Natta and M. Strada's observations on the X-ray spectral lines are summarized in Fig. 72. The hydrate could not be obtained in a definite crystalline form, and the X-radiograms show the lines of cobaltic oxide which is formed on dehydration. G. Natta and M. Strada, G. F. Hüttig and R. Kassler, and F. Merck and E. Wedekind found that all preparations between  $\text{Co}_2\text{O}_3$  and  $\text{Co}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  have the same  $\text{Co}_2\text{O}_3$  lines. A. Coehn and M. Gläser, and W. Wernicke gave values for the sp. gr. of the hydrate. G. Natta and M. Strada found 4.29 to 4.90 for the sp. gr. of  $\text{Co}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ , and 4.46 to 4.47 for  $2\text{Co}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ . According to G. C. Winkelblech, when the hydrates are heated, water is first evolved, then oxygen and water, until cobaltous oxide is formed which does not part with the remaining water until a red-heat is attained. G. Natta and M. Strada said that the hydrate passes into anhydrous  $\text{Co}_2\text{O}_3$  if it be heated below  $250^{\circ}$ —*vide supra*. According to T. Carnelley and J. Walker, the air-dried precipitate has the composition:  $5\text{Co}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$ , and it retained this composition when heated for 6 hrs. at temp. ranging up to  $74^{\circ}$ . When heated beyond this, it gradually lost water, and at  $100^{\circ}$ , it had the composition:  $2\text{Co}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ . This, however, represented a chance stage in a continuous process, for the water was lost continuously up to  $260^{\circ}$  without any evidence of the formation of a stable hydrate. The loss of water was now rapid, and the composition at  $270^{\circ}$  approximated  $10\text{Co}_2\text{O}_3 \cdot \text{H}_2\text{O}$ , and remained almost constant between  $280^{\circ}$  and  $360^{\circ}$ , when a further loss occurred. Dehydration was complete at  $385^{\circ}$ , but, as the last traces of water were expelled, there was also a slight loss of oxygen with the corresponding formation of cobaltous oxide. G. F. Hüttig and R. Kassler obtained the dehydration curves of the hydrated cobaltic oxides, at 10 mm. press., when the oxides were prepared in different ways. The results, Fig. 74, show that when the mol. ratio of water to oxide is less than 3, the water is held more tenaciously than would be expected on the assumption of adhesion or capillarity. Dehydration between the limits 3 : 1 and 1 : 1 increases smoothly with rise of temperature, and the ease with which the water can be removed varies with the mode of preparation. No evidence of the

existence of a definite compound intermediate between a mono- and a trihydrate has been obtained. Removal of water from a product having the composition  $\text{Co}_2\text{O}_3 \cdot \text{H}_2\text{O}$  takes place at constant temperature, and is usually accompanied by the formation of cobalto-cobaltic oxide. The existence of a definite monohydrate is indicated, and this is supported by the X-radiograms. The last 0.3 mol. of water requires a temp. over  $300^\circ$  before it is expelled.

T. Carnelley and J. Walker observed that the dehydration is almost complete at  $280^\circ$ , and C. F. Cross, and G. C. Winkelblech found that a red-heat is necessary to drive off all the water. According to the f.p. determinations of G. Urbain and A. Debiere, the formula of cobalt acetylacetonate,  $\text{Co}\{\text{CH}(\text{COCH}_3)_2\}_3$ , corresponds with  $\text{Co}(\text{OH})_3$  rather than with  $\text{Co}_2(\text{OH})_6$ . J. Thomsen found the heat of formation  $(2\text{Co}_2\text{O}_3, 3\text{H}_2\text{O}) = 149.3$  Cals.; and  $(2\text{Co}(\text{OH})_2, \text{O}, \text{H}_2\text{O}) = 22.58$  Cals. A. H. Barnes studied the X-ray absorption spectrum. G. Grube and O. Feucht gave 0.109 volt for the potential in 8N-KOH at  $25^\circ$ ; and E. Müller and F. Spitzer, 0.4 volt for an anode covered with  $\text{Co}_2\text{O}_3 \cdot n\text{H}_2\text{O}$  in ammoniacal soda-lye. E. H. Williams said that the oxide is paramagnetic. A. Quartaroli found the magnetic susceptibility to be  $7 \times 10^{-6}$  to  $25 \times 10^{-6}$  mass unit; F. Merck and E. Wedekind gave  $7.95 \times 10^{-6}$  mass unit for  $\text{Co}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ , and zero for  $\text{Co}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ; and P. Hausknecht gave  $2.7 \times 10^{-6}$  mass unit for  $2\text{Co}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ . S. Veil found that the mol. coeff. of magnetization rises to a maximum as the cobaltic hydroxide is repeatedly re-dissolved and re-precipitated, or treated with hot water; F. Merck and E. Wedekind studied the change in the magnetic susceptibility which occurs on heating different preparations of the hydrated oxide.

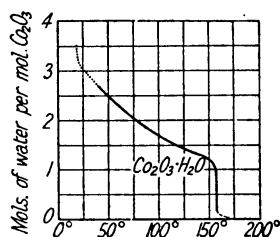


FIG. 74.—Dehydration Curve of Hydrated Cobaltic Oxide.

A. F. Benton observed that **helium** is not absorbed by the hydroxide; but at  $-79^\circ$  a gram of the oxide absorbs 0.325 c.c. of **hydrogen** at n.p.  $\theta$ . H. Moissan observed that when hydrated cobaltic oxide is heated in hydrogen, it loses water between  $100^\circ$  and  $200^\circ$ , and reduction to cobalt begins at about  $250^\circ$ . C. R. A. Wright and A. P. Luff said that the reduction begins at  $110^\circ$ . A. F. Benton found that 0.325 vol. of hydrogen at n.p.  $\theta$  is absorbed by cobaltic oxide at  $-79^\circ$ ; and of **oxygen**, 0.264 at  $0^\circ$ ; 0.116 at  $56.5^\circ$ ; and 0.073 at  $110^\circ$ . G. Schröder found that oxygen at a red-heat has no action on cobaltic oxide. A. Coehn and M. Gläser, C. F. Cross, and G. Natta and M. Strada noted the great hygroscopicity of the hydrated oxide in **air**. E. Saint-Evre observed that the hydroxide is slightly soluble in hot **water**; and at  $20^\circ$ , G. Almkvist found that water containing carbon dioxide dissolves 3.18 mgrms. per litre. F. G. Tryhorn and G. Jessop studied the action of the colloid on **hydrogen dioxide**. Observations on the effect of acids have been made by W. Beetz, M. le Blanc and J. E. Möbius, C. D. Braun, A. Coehn and M. Gläser, E. Donath, E. Donath and J. Mayrhofer, W. Hempel and H. Thiele, E. Hüttner, F. Mawrow, S. W. Parr, J. L. Proust, A. Remelé, J. B. Rogojsky, E. Saint-Evre, F. W. Skirrow, F. G. Tryhorn and G. Jessop, W. Wernicke, and G. C. Winkelblech. The hydrated oxide is readily dissolved by **hydrofluoric acid**. As indicated by J. L. Proust, the hydrates dissolve in hot **hydrochloric acid**, with the evolution of chlorine; and G. C. Winkelblech noted that the hydrate dissolves in cold hydrochloric acid in the dark, but on exposure to light, or heat, chlorine gas is evolved and cobaltous chloride is formed. G. C. Winkelblech observed that when the hydrated oxide is warmed with a **hypochlorite**, oxygen is evolved. O. R. Howell studied the reaction. The hydrate is dissolved by **hydriodic acid** with the separation of iodine; and G. C. Winkelblech found that it forms a reddish-yellow liquid with a soln. of **sodium iodide**. J. L. Proust said that cobaltic oxide dissolves in **sulphurous acid**, with the formation of cobaltous sulphate. A. Geuther found that the freshly-precipitated hydrate dissolves in a warm soln. of **ammonium**

**sulphite**, with the evolution of ammonia, and the formation of a soln. of cobalt-ammine; and similarly with soln. of **potassium or sodium sulphite**. S. R. Benedict said that soln. of potassium **hydrosulphate** reduce the oxide. J. L. Proust also observed that the hydrate dissolves in warm **sulphuric acid**, with the evolution of oxygen. G. C. Winkelblech observed that in the dark, the oxide may be dissolved in cold sulphuric acid, but on exposure to light or heat, decomposition occurs, with the evolution of oxygen and the formation of a soln. of cobaltous sulphate. J. L. Proust, and G. C. Winkelblech observed that hydrated cobaltic oxide is not decomposed by aq. **ammonia**, even when warmed, and dissolution occurs only in the presence of a piece of tin. The resulting liquid is red. E. Donath and J. Mayrhofer, E. Fleischer, E. Hüttner, H. Rose, L. J. Thénard, T. Vorster, and G. C. Winkelblech said that the hydroxide is insoluble in aq. ammonia; on the other hand, O. W. Gibbs and F. A. Genth, and H. Remmler said that the hydrate is soluble in aq. ammonia—*vide infra*, aminohydroxides. T. Vorster found that the hydrate is not changed when it is heated with aq. or alcoholic ammonia in a sealed tube, or heated in the dry gas, at 170°. E. Donath and J. Mayrhofer observed that the hydroxide is insoluble in an aq. soln. of **ammonium chloride**, but if ammonia is added and the mixture is warmed, C. D. Braun said that the hydrated oxide dissolves; and E. J. Mills, and O. W. Gibbs and F. A. Genth observed that in a sealed tube at 70°, amines are formed. A. Geuther noted that the hydrated oxide dissolves slowly in a soln. of **ammonium sulphite** in the cold, and if heated, an ammine is formed. J. Mai and M. Silberberg said that hydrated cobaltic oxide is more stable towards **hydroxylamine** than is the case with nickelic oxide. A. Geuther observed that a neutral soln. of **potassium nitrite** does not change hydrated cobaltic oxide, but if a few drops of acid are added, yellow potassium cobaltic nitrite is formed. J. L. Proust observed that the hydrated oxide dissolves in fuming **nitric acid**, forming cobaltous nitrate, and it dissolves in warm nitric acid, with the evolution of oxygen. G. C. Winkelblech said that the dissolution of the hydrate in cold nitric acid in the dark is slow, and on exposure to light or heat, oxygen is evolved; and a similar observation was made with respect to **phosphoric acid**. G. C. Winkelblech said that with soln. of **alkali phosphate**, a brown precipitate is formed. C. Reichard found that a soln. of **arsenic trioxide** in soda-lye turns hydrated cobaltic oxide yellowish-brown in the cold, and when heated, greyish-brown, and finally dark blue; an ammoniacal soln. of arsenic trioxide reduces hydrated cobaltic oxide, and similarly with an aq. soln. G. C. Winkelblech said that with soln. of **alkali arsenite**, a brown precipitate is formed. With alkali oxalate, G. C. Winkelblech observed that a green soln. is formed; and F. Kehrmann, that in the presence of free acid, a complex salt is produced. C. R. A. Wright and A. P. Luff observed that **carbon** begins to reduce the hydrated oxide at 260°, and **carbon monoxide**, at -11°. F. Merck and E. Wedekind found that whilst hydrated cobaltic oxide—presumably  $\text{Co}_3\text{O}_4 + \text{CoO}(\text{OH})$ —is almost inert in the catalytic oxidation of carbon monoxide at ordinary temp., the oxide is activated by the addition of manganese dioxide, and they examined the magnetic properties of the mixtures. A. F. Benton found that a gram of oxide at -79° absorbs 6 c.c. of carbon monoxide. C. J. Engelder and M. Blumer studied the catalytic activity of mixtures of cobaltic and ferric oxides in the oxidation of carbon monoxide. A. F. Benton observed that at 0°, 56.5°, and 100°, 1 gram of the oxide adsorbs, respectively, 10.21, 5.09, and 2.46 c.c. of **carbon dioxide**, at n.p.  $\theta$ . W. P. Yant and C. O. Hawk studied the catalytic effect of the oxide on the oxidation of **methane**. A. Jorissen, and C. Reichard found hydrated cobaltic oxide does not dissolve in a soln. of **potassium cyanide**; but C. Krause, and E. Fleischer said that dissolution does take place. G. C. Winkelblech said that with soln. of **potassium ferrocyanide**, a dark red precipitate is formed. J. Mai and M. Silberberg observed that the hydrated oxide is more stable than nickelic oxide when in contact with **potassium or ammonium thiocyanate**. The solubility of the hydrated oxide in organic acids was studied by W. Beetz, M. le Blanc and J. E. Möbius, E. Fleischer, E. Hüttner,

F. Kehrmann, F. Mawrow, A. Remelé, E. Saint-Evre, A. Stromeyer, and G. C. Winkelblech. A. Remelé observed that conc. **acetic acid** dissolves hydrated cobaltic oxide without immediate decomposition, forming a brown soln.; and in oxalic acid, a green soln. is formed and carbon dioxide is evolved. G. C. Winkelblech observed that the hydrated oxide is soluble in **racemic, tartaric, oxalic, or citric acids**, forming cobaltous salts. N. Orloff observed that the soln. of hydrated cobaltic oxide in organic acids—*e.g.*, acetic or oxalic acid—soon decompose. A mixture of oxalic acid and ammonium acetate forms ammonium cobaltic oxalate. G. C. Winkelblech found that with a hot, aq. soln. of oxalic acid, cobaltous oxalate is formed, with the evolution of carbon dioxide; and if the moist, fresh hydrated oxide is heated with a soln. of **ammonium oxalate**, ammonia is evolved, and a green soln. of cobaltous oxalate is formed. A. H. Allen found that the hydrated oxide is stable in contact with **glycerol**; and E. Donath observed that freshly-precipitated hydrated cobaltic oxide is very slowly decomposed by a soln. of glycerol and soda-lye, or of glycerol, and ammonia, whilst with nickelic oxide under similar conditions a blue soln. is quickly formed, and the reaction can be utilized to detect cobalt in the presence of nickel.

H. Hess found that molten **potassium hydroxide** dissolves the hydrated oxide, forming an intense brown mass, but E. Hüttner said that the hydrated oxide is not attacked by alkali-lye. G. Schröder observed that with soln. of **manganese salts**, or of **ferric salts**, a basic salt is produced. P. Louyet, and E. Fischer found that with soln. of **ferrous salts**, the hydrated cobaltic oxide is reduced to cobaltous oxide, and hydrated ferric oxide is precipitated.

**The salts of cobaltic oxide.**—Cobaltic oxide is an amphoteric oxide, forming unstable salts with acids, and with bases. Solutions of the hydrated oxide in acids may not decompose immediately, and they then contain, presumably, **cobaltic salts**, but the soln. quickly decomposes, forming cobaltous salts with the evolution of oxygen. This was shown by G. C. Winkelblech to be the case with cold phosphoric, sulphuric, nitric, and hydrochloric acids, but best of all with cold acetic acid. W. Beetz, and N. Orloff also obtained similar results with acetic and oxalic acids. G. C. Winkelblech observed that the colour of a cobaltous salt appears darker if some cobaltic salt is present. The brown soln. of cobaltic acetate gives a brown precipitate with potassium hydroxide or carbonate, or with ammonium carbonate; the precipitation is incomplete with aq. ammonia—perhaps owing to the formation of an *ammonium cobaltite*,  $(\text{NH}_4)_2\text{O} \cdot \text{Co}_2\text{O}_3$ , or  $(\text{NH}_4)\text{CoO}_2$ . Sodium iodide gives a reddish-yellow soln., and alkali oxalates, a yellow soln. Hydrogen sulphide, and ammonium sulphide give black precipitates; alkali phosphates, and arsenates, brown precipitates; and potassium ferrocyanide gives a dark red precipitate—if the precipitant is in excess, potassium ferricyanide and green cobalt ferricyanide may be formed. The ferrocyanide precipitate was studied by C. D. Braun, and A. Remelé. For O. Feucht and G. Grube's, and G. Grube's observations on **potassium cobaltite**,  $\text{K}_2\text{CoO}_2$ , *vide supra*, anodic behaviour of cobalt.

There is a series of compounds of the spinel type formed by the union of a bivalent metal oxide, which acts as a base, with oxide of a trivalent metal—*e.g.*, aluminium, chromium, and ferric iron—which acts as an acidic oxide, to form  $\text{R}''\text{O} \cdot \text{R}_2'''\text{O}_3$ , or  $\text{R}''(\text{R}'''\text{O}_2)_2'$ . Cobaltic oxide also forms analogous spinels. S. Holgersson and A. Karlsson prepared a series of **cobaltites** by evaporating to dryness mixed soln. of cobalt nitrate and a nitrate of the bivalent metal, and heating the mixture to  $850^\circ$  for  $1\frac{1}{2}$  hrs.

W. G. Mixer was not able to isolate **sodium cobaltite**,  $\text{Na}_2\text{O} \cdot \text{Co}_2\text{O}_3$ , or  $\text{NaCoO}_2$ , but he supposed that it is present in the product obtained by fusing cobalt oxide with an excess of sodium dioxide. The blue soln. of sodium cobaltite obtained by dissolving cobaltous oxide, or hydroxide, in conc. soda-lye, behaves just like a soln. of potassium cobaltite—*vide supra*, in connection with cobaltic oxide. R. Scholder and H. Weber prepared sodium cobaltite from solutions of cobalt nitrate and sodium hydroxide. The product was  $\text{Na}_2[\text{Co}(\text{OH})_4]$ , or  $\text{Na}_2\text{CoO}_2 \cdot 2\text{H}_2\text{O}$ .

A. C. Becquerel, I. Bellucci and F. Dominici, H. Hess, W. Mayer, L. Pebal, and A. Schwarzenberg noted the formation of **potassium cobaltite**, say in the ideal case,  $\text{K}_2\text{CoO}_2$ , by melting potassium hydroxide with a cobalt salt. A. Schwarzenberg gave  $\text{K}_2\text{O} \cdot 3\text{Co}_3\text{O}_5 \cdot 3\text{H}_2\text{O}$ ; L. Pebal,  $\text{K}_2\text{O} \cdot 2\text{Co}_3\text{O}_5$ ; I. Bellucci and F. Dominici,  $\text{K}_2\text{Co}_4\text{O}_8$ ; and W. Mayer added that the alkali is not present in stoichiometrical proportions. I. Bellucci and F. Dominici noted that the product is hydrolyzed by water, so that by repeated washing, A. H. McConnell and E. S. Hanes, and O. Brunck obtained cobaltous oxide,  $\text{Co}_3\text{O}_4$ , as a residue. L. E. R. Dufau, and J. A. Hedvall observed no formation of a calcium cobaltite when mixtures of cobaltic and calcium oxides are heated together; and similarly with **strontium cobaltite**. R. Scholder and H. Weber also obtained  $\text{Sr}_2[\text{Co}(\text{OH})_6]$ . J. A. Hedvall and N. von Zweigbergk obtained **barium cobaltite** by the action of barium dioxide on cobalt oxide. G. Rousseau obtained crystalline products,  $\text{BaO} \cdot 2\text{CoO}_2$ , and  $\text{BaO} \cdot \text{CoO}_2$ —*vide infra*, percobaltites. R. Scholder and H. Weber also obtained  $\text{Ba}_2[\text{Co}(\text{OH})_6]$ .

S. Holgersson and A. Karlsson obtained **copper cobaltite**,  $\text{Cu}(\text{CoO}_2)_2$ . The X-radiograms show that the spinel lattice has 8 mols. per unit cell, and that the edge of unit cell is 8.039 Å., and the sp. gr. 6.28. It showed no ferromagnetism. The corresponding **magnesium cobaltite**,  $\text{Mg}(\text{CoO}_2)_2$ , has a spinel lattice with edge 8.107 Å., and sp. gr. 4.96. It shows no ferromagnetic properties. J. A. Hedvall, S. Holgersson and A. Karlsson, L. Passerini, G. Natta and L. Passerini, and L. E. R. Dufau, H. J. Witteveen and E. F. Farnau also prepared this salt.

G. Natta and M. Strada prepared **zinc cobaltite**,  $\text{ZnO} \cdot \text{Co}_2\text{O}_3$ , or  $\text{Zn}(\text{CoO}_2)_2$ , by evaporating a soln. of mixed zinc and cobalt nitrates to dryness, and calcining the product at  $800^\circ$ . G. Natta and L. Passerini found that cobaltous and zinc oxide form solid soln. at temp. exceeding  $1000^\circ$ , but below that temp., in an oxidizing atm., zinc cobaltite,  $\text{Zn}(\text{CoO}_2)_2$ , is formed. It was studied by J. A. Hedvall and co-workers, and G. Natta and co-workers, and S. Holgersson and co-workers—*vide supra*, Rinman's green, cobaltous and zinc oxides. S. Holgersson and A. Karlsson gave for the zinc cobaltite lattice  $a=8.108$  Å., and the sp. gr. 5.94. G. Natta and M. Strada gave  $a=8.06$  Å., and sp. gr. 6.11. The salt showed no ferromagnetism. S. Holgersson and A. Karlsson also prepared a **manganous cobaltite**,  $\text{Mn}(\text{CoO}_2)_2$ , but in which some cobalt took the place of bivalent manganese, and some manganese in place of trivalent cobalt. The lattice constant is of the spinel type with  $a=8.268$  Å. It did not exhibit ferromagnetism. A. Serres measured the magnetic susceptibility between  $-182.7^\circ$  and  $549.4^\circ$ ; the Curie point is  $-164.5^\circ$ ; the Curie constant, 4.261; and the magnetic moment for quadrivalent cobalt, 29. The cobaltites are isomorphous with cobaltous oxide, which can accordingly be regarded as **cobaltous cobaltite**,  $\text{Co}(\text{CoO}_2)_2$ . The cubic lattice of this salt is of the spinel type with the parameter  $a=8.06$  Å. The calculated density is 6.27. S. Holgersson and A. Karlsson gave  $a=8.108$  Å., and S. Holgersson,  $a=8.110$  Å. The corresponding **nickel cobaltite**,  $\text{Ni}(\text{CoO}_2)_2$ , has a cubic lattice of the sodium chloride type, with  $a=8.112$  Å. Bivalent cobalt may replace some of the nickel, and trivalent nickel, some of the cobalt. The compound is strongly ferromagnetic.

**The cobaltic aminohydroxides.**—E. Frémy<sup>2</sup> obtained an aq. soln. of **cobaltic hexamminohydroxide**,  $[\text{Co}(\text{NH}_3)_6](\text{OH})_3$ , by the action of barium hydroxide on a soln. of the sulphate. O. W. Gibbs and F. A. Genth, and L. Jacobsen prepared the compound by similar processes. The compound cannot be isolated by evaporating the yellowish-brown liquid, since decomposition with the evolution of ammonia sets in. A. B. Lamb and co-workers gave for the molecular conductivity,  $\mu$ , and percentage ionization,  $\alpha$ , of soln. with  $C$  mols. per litre at  $0^\circ$  and  $25^\circ$ :

0°					25°			
$C$	33.23	6.662	1.336	0.2678	33.23	6.662	1.336	0.2678
$\mu$	347.5	396.9	431.1	469.0	591.3	675.3	739.0	843.0
$\alpha$	72.2	82.4	89.5	97.4	65.5	74.8	81.8	93.4

S. M. Jørgensen prepared **cobaltic trisethylenediaminehydroxide**,  $[\text{Co en}_3](\text{OH})_3$ , where en is employed for  $\text{C}_2\text{H}_4(\text{NH}_2)_2$ . The compound is obtained by shaking freshly-precipitated silver oxide with the corresponding chloride, and evaporating the soln., finally, over sulphuric acid. The dark yellow mass of deliquescent crystals furnishes an orange-yellow liquid. A. B. Lamb and co-workers measured the mol. conductivity, and found for soln. with 33.29 and 0.2683 mol. per litre, the respective conductivities 304.2 and 706.8 at  $0^\circ$ , and 394.4 and 519.1 at  $25^\circ$ ; the corresponding percentage degrees of ionization are 67 and 93 at  $0^\circ$ , and 66.4 and 90.4 at  $25^\circ$ . P. Pfeiffer and T. Gassmann obtained **cobaltic trispropylenediaminehydroxide**,  $[\text{Co pn}_3](\text{OH})_3$ , in aq. soln. by shaking the iodide of the series with freshly-precipitated silver oxide in water. The hydroxide was not isolated. Similarly also with **cobaltic ethylenediaminebispropylenediaminehydroxide**,  $[\text{Co en}_2\text{pn}](\text{OH})_3$ .

O. W. Gibbs and F. A. Genth obtained **cobaltic aquopentamminohydroxide**,  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})](\text{OH})_3$ , by treating a soln. of the chloride of the series with silver oxide, or the sulphate with barium hydroxide. The compound is known only in aq. soln. S. M. Jørgensen prepared it by treating chloropentamminochloride with silver oxide, or chloropentamminosulphate with barium hydroxide. N. R. Dhar used a similar process. A. B. Lamb and co-workers measured the mol. conductivity,  $\mu$ , of aq. soln. of  $C$  mols. of the compound per litre, and calculated  $\alpha$ , the percentage ionization on the assumption that the complex contains  $\text{H}_2\text{O}$ , and  $\alpha'$ , for the assumption that the complex contains  $\text{OH}$  :

$C \times 10^3$	.	.	.	33.21	6.66	1.335	0.2683
$\mu$	.	.	.	223.4	244.7	261.8	286.8
$\alpha$	.	.	.	45.7	55.0	53.5	58.6
$\alpha'$	.	.	.	70.8	77.9	82.9	92.7

at the limit  $\mu_\infty = 296$  at  $0^\circ$ . They inferred that the compound is more likely to be a hydroxypentammine than an aquopentammine. H. J. S. King also studied this compound. A. B. Lamb and co-workers, and H. J. S. King obtained a soln. of **cobaltic diaquotetramminohydroxide**,  $[\text{Co}(\text{H}_2\text{O})_2(\text{NH}_3)_4](\text{OH})_3$ , but not the solid. The mol. conductivity,  $\mu$ , at  $0^\circ$ , and the percentage ionization,  $\alpha$ , on the assumption that the complex contains  $2\text{H}_2\text{O}$ -groups, and  $\alpha'$ , on the assumption that it contains  $2\text{OH}$ -groups, for soln. with  $C$  mols. per litre, are :

$C \times 10^3$	.	.	.	6.59	1.321	0.265
$\mu$	.	.	.	116.4	115.4	102.7
$\alpha$	.	.	.	24.8	24.5	21.8
$\alpha'$	.	.	.	74.7	74.0	65.9

where at the limit  $\mu = 469.0$  at  $0^\circ$  for the aquo-complex, and 154.0 for the hydroxide complex. The results favour the assumption that the compound is not a diaquotetrammine, but a hydroxytetrammine.

A. B. Lamb and co-workers found that **cobaltic diaquobisethylene diaminehydroxide**,  $[\text{Co en}_2(\text{H}_2\text{O})_2](\text{OH})_3$ , is stable only in aq. soln., and that the mol. conductivity,  $\mu$ , of soln. with  $C$  mols per litre, and the percentage ionization calculated  $\alpha$  on the assumption that the complex contains  $2\text{H}_2\text{O}$ -groups, and  $\alpha'$  on the assumption that it contains  $2\text{OH}$ -groups, are :

$C \times 10^3$	.	.	.	33.2	6.674	1.338	0.2683
$\mu$ at $25^\circ$	.	.	.	185.0	197.4	209.0	269.4
$\alpha$ at $25^\circ$	.	.	.	22.7	25.2	26.7	34.5
$\mu$ at $0^\circ$	.	.	.	107.6	113.9	116.8	143.1
$\alpha$ at $0^\circ$	.	.	.	24.6	26.6	27.3	33.4
$\alpha'$	.	.	.	73.7	79.8	81.8	100.3

where the limiting value of  $\mu = 430$  at  $0^\circ$  on the assumption that  $2\text{HO}$ -groups are present in the complex ion, and 115.0 on the assumption that the complex ion contains  $2\text{H}_2\text{O}$ -groups. The results favour the assumption that the compound is a dihydroxy-salt not a diaquo-salt. The subject was discussed by H. J. S. King.

P. Job prepared a soln. of **cobaltic hydroxypentamminohydroxide**,  $[\text{Co}(\text{NH}_3)_5(\text{OH})](\text{OH})_2$ , by treating the corresponding sulphate with the theoretical

proportion of barium hydroxide. The hydroxide is not precipitated by alcohol.

A. Job, and H. J. S. King prepared **cobaltic dihydroxytetramminohydroxide**,  $[\text{Co}(\text{NH}_3)_4(\text{OH})_2](\text{OH})$ , and found for the eq. conductivity,  $\lambda$ , at  $0^\circ$ , of soln. with an eq. of the salt in  $v$  litres :

$v$	31.23	65.96	125.0	263.8	511.0	1002	$\infty$
$\lambda$	118.0	120.6	122.2	123.6	123.0	116.6	126.6

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### § 13. The Higher Oxides of Cobalt—Cobalt Dioxide

G. C. Winkelblech,<sup>1</sup> E. Frémy, O. Brunck, G. Schröder, and G. Natta and M. Strada were not able to prepare **cobalt dioxide**,  $\text{CoO}_2$ , in the dry way; and J. A. Hedvall and N. von Zweigbergk noted the formation of a peroxide when cobalt oxide is heated with barium dioxide. The dioxide appears associated with more or less cobaltous oxide, so that the various oxides between cobaltic oxide,  $\text{Co}_2\text{O}_3$ , or possibly cobaltous oxide,  $\text{CoO}$ , and cobalt dioxide,  $\text{CoO}_2$ , which have been reported, are probably mixtures or solid soln. of cobaltous oxide and cobalt dioxide. Indeed, cobaltic oxide, as reported in some cases, may be a mixture of the two oxides,  $\text{CoO} \cdot \text{CoO}_2$ , or possibly *cobaltous percobaltite*,  $\text{Co}(\text{CoO}_3)$ . The methods employed for preparing the dioxide have a marked influence on the composition of the final product. In some cases the oxide,  $m\text{CoO} \cdot n\text{CoO}_2$ , actually obtained, probably represents an arrested reaction (**4**, 31, 33), an accidental stage in the degradation of cobalt dioxide to cobaltous oxide. Our knowledge of the higher oxides of cobalt is not in a satisfactory state. A. Quartaroli inferred the existence of higher oxides from measurements of the magnetic susceptibilities of the oxidized products. R. Bernard and P. Job believed that the dioxide is formed as an intermediate stage in the oxidation of cobaltous to cobaltic oxide.

E. Hüttner observed that when cobalt sulphate is oxidized by potassium persulphate in acidic or alkaline soln., by ammonium persulphate in alkaline soln., by chlorine gas, or by anodic chlorine from a soln. of cobalt sulphate containing a large excess of potassium chloride, the product always approximates to cobaltic oxide,  $\text{Co}_2\text{O}_3$ , but by the direct application of hypochlorites, a higher oxide can be obtained. Thus, J. Thomsen prepared a hydrate approximately  $\text{Co}_3\text{O}_5$ , or  $\text{CoO}_{1.70}$ , by the action of equimolar parts of sodium hypochlorite and cobaltous chloride, and if the action be allowed to continue for a long time, the product approximates  $\text{Co}_3\text{O}_7$ , or  $\text{CoO}_{1.75}$ . T. Bayley obtained, in an analogous manner, a precipitate approximating  $\text{Co}_3\text{O}_5$ , and with hot soln., the product had rather less oxygen,  $\text{Co}_{12}\text{O}_{19}$ , or  $\text{CoO}_{1.6}$ ; using boiling soln., G. Schröder obtained  $\text{Co}_5\text{O}_8 \cdot 11\text{H}_2\text{O}$ , that is, hydrated  $\text{CoO}_{1.6}$ . A. Carnot, with hypochlorites in alkaline soln., obtained oxides ranging from  $\text{CoO}_{1.60}$  to  $\text{CoO}_{1.625}$ ; and E. Hüttner, using a dil. soln. of a cobalt salt and an excess of oxidizing agent, found that the product fell from  $\text{CoO}_{1.6}$  to  $\text{CoO}_{1.575}$ . Analogous oxidation products, exceeding  $\text{Co}_2\text{O}_3$ , were obtained by C. Krause, O. R. Howell, H. McLeod, E. Fleischer, G. Schröder, O. Popp, T. Bayley, R. Fischer, G. Vortmann, and A. Metzl, with a hypochlorite as oxidizing agent. The existence of a hypothetical acid,  $\text{H}_2\text{CoO}_3$ , was assumed by H. Copaux, R. G. Durrant, A. Job, A. H. McConnell and E. S. Hanes, and C. Winkler.

O. R. Howell studied the action of hypochlorites on soln. of cobalt sulphate, and

found that hypochlorites free from alkali immediately precipitate from aq. soln. of cobalt sulphate a slightly peroxidized cobalt sesquioxide of constant composition; but since the peroxide catalytically decomposes the hypochlorite, the precipitation is far from quantitative. When less than half an eq. of hypochlorite is used with an excess of alkali, more available oxygen is found in the precipitate than was used in the hypochlorite; this is attributed to atm. oxidation of the precipitated hydroxide. A higher degree of oxidation is reached with hypochlorite and alkali than with hypochlorite alone. This is attributed to the formation of a hydroxylated peroxide, by the direct oxidation of cobaltous hydroxide. The temp. has no important influence on the composition of the precipitate. The oxide is very stable, since it can be kept indefinitely, and prolonged boiling causes no loss of available oxygen. The concentration of the reacting solutions likewise has practically no influence on the composition of the precipitate.

A fully-oxidized precipitate was obtained by precipitating cobalt sulphate with sodium hydroxide and hypochlorite, using 1.5 eq. of alkali hydroxide per eq. of hypochlorite; when the decomposition of the excess of hypochlorite was complete, another eq. was added; and after the decomposition of this, another 0.5 eq. was added. The precipitate was allowed to settle, washed by decantation three times, filtered and washed on a Buchner funnel until the filtrate was almost free from alkali. The deposit was then shaken up with water and allowed to stand in contact with water 3 months before use.

O. R. Howell compared the oxidation of nickel and cobalt salts by hypochlorites, and found that the peroxidized precipitate obtained with cobalt is stable; it can be kept for a long time, or the suspension boiled without loss of oxygen. With nickel, the precipitate decomposes with evolution of oxygen even in suspension at the ordinary temperature, and the oxygen content falls continuously below that corresponding to the sesquioxide; decomposition is accelerated by heat and retarded by alkali. Hypochlorites free from alkali react immediately with cobalt solutions, yielding a peroxidized precipitate, the rate of the reaction being comparable with that of precipitation of the hydroxide by alkali and its oxidation by hypochlorite. With nickel, the action is delayed and is negligibly slow compared with the action in the presence of alkali. In the presence of alkali, the hydroxides are peroxidized. With cobalt, excess of hypochlorite causes a decrease in the oxygen-content owing to its further oxidizing action. With cobalt, excess of alkali causes a small increase in the oxygen-content owing to increased precipitation as hydroxide; with nickel, it causes a large increase owing to its retarding decomposition of the precipitate. Precipitated with sodium carbonate and hypochlorite, cobalt salts yield a peroxidized carbonate; in the case of nickel, however, the precipitated carbonate is oxidized to the peroxide with a loss of carbon dioxide, which yields the bicarbonate.

R. Fischer oxidized cobalt salts with bromine in the presence of an alkali, and obtained products similar to those obtained with the hypochlorites. Analogous results were obtained by E. Fleischer, A. Carnot, E. Donath and J. Mayrhofer, and R. Fischer, by using iodine or bromine as oxidizing agent in alkaline soln. G. Vortmann oxidized a soln. of cobalt sulphate with iodine and alkali-lye, and obtained products ranging from  $\text{CoO}_{1.7}$  to  $\text{CoO}_{1.8}$ . E. Hüttner observed that when an alkaline soln. of potassium cobalt sulphate is oxidized with an excess of iodine, the black precipitate approximates closely to  $\text{CoO}_2$ . If less iodine be employed, a less highly-oxidized product is obtained. A. Metzl observed that cobalt dioxide can be prepared by mixing cobalt sulphate, iodine, and alkali-lye, washing the precipitate by decantation, and filtering through asbestos in order to avoid reduction by the filter-paper. The same compound was obtained by using silver nitrate and alkali-lye as oxidizing agent, as did H. Rose, in 1857. The silver which is precipitated—possibly as  $\text{Ag}_4\text{O} \cdot \text{Co}_2\text{O}_3$  (H. Rose)—can be removed by washing with permanganate and nitric acid.

C. Tubandt oxidized a blue soln. of cobaltous hydroxide in potash-lye, using a porous diaphragm, and obtained about the anode, a bluish-black oxide approxi-

inating  $\text{CoO}_{1.6}$ . The anodic oxidation of cobalt in potash-lye at high current-densities was shown by G. Grube and O. Feucht, A. Coehn and E. Salomon, H. N. Holmes, N. Isgarischeff, and E. Müller and F. Spitzer to furnish a solid soln. of cobalt dioxide in one of the lower oxides—*vide supra*, hydrated cobaltic oxide. K. A. Hofmann and H. Hiendlmaier fused cobaltous oxide with potassium dioxide, washed the product with water for several days, digested it with cold, 10 per cent. sulphuric acid, again washed the product with water, and then dried it over phosphorus pentoxide. The tabular crystals had a composition corresponding with  $\text{Co}_3\text{O}_5 \cdot 2\text{H}_2\text{O}$ , or hydrated  $\text{CoO}_{1.67}$ . A. H. McConnell and E. S. Hanes said that the *monohydrate*,  $\text{CoO}_2 \cdot \text{H}_2\text{O}$ , or  $\text{H}_2\text{CoO}_3$ , is formed by the action of hydrogen dioxide on cobaltous hydroxide suspended in water, but R. G. Durrant could not confirm this. A. Metz observed that the oxidation of a cobalt salt soln. by hydrogen dioxide and sodium hydrocarbonate furnishes a green precipitate, which, when analyzed in the moist state, has the composition  $\text{Co}_2\text{O}_3 \cdot \text{CoCO}_3$ , or  $\text{Co}(\text{CoO}_3) \cdot \text{CoCO}_3$ . B. Brauner used potassium permanganate as oxidizing agent; D. Bhaduri and P. Ray, potassium ferricyanide; and F. Fichter and A. R. y Miro, potassium perphosphate.

G. Schröder obtained a colloidal soln. of  $\text{Co}_3\text{O}_5$  by digesting the freshly-precipitated oxide with nitric acid for some days, and then washing with water. The precipitate is peptized, and a clear, dark brown soln. is formed. The sol. coagulates and becomes turbid after standing for 10 days. The sol. is also coagulated by the addition of alkali salts.

The product obtained by precipitation methods is usually black; that obtained by K. A. Hofmann and H. Hiendlmaier appeared in 6-sided plates, sometimes arranged in rosettes. S. Veil studied the magnetic properties of cobalt hydroxide which had been treated with hydrogen dioxide. The general properties of these oxides resemble those of hydrated cobaltic oxide. With hydrochloric acid, chlorine is given off, and with sulphuric acid, oxygen. According to O. R. Howell, the rate of decomposition of sodium hypochlorite by cobalt peroxide has been investigated at  $25^\circ$  and  $50^\circ$  under various conditions. It has shown that the rate of decomposition is directly proportional to the quantity of cobalt peroxide present. The rate of decomposition is accelerated by the presence of sodium salts; in the case of sodium chloride it is directly proportional to the square root of the concentration of sodium-ions present. This is explained by assuming the mechanism of the reaction to consist in the linking of hypochlorite-ions to the positive oxygen, and sodium-ions to the negative oxygen of the peroxide, with subsequent immediate decomposition of the quadrivalent oxygen compound. In the presence of a fixed amount of hypochlorite, the rate is then proportional to the degree of adsorption of the sodium-ions. The rate is retarded by alkali, and the retardation is proportional to the adsorption of hydroxyl-ions. This is attributed to the hydroxyl-ions being attracted by the positive oxygen of the peroxide, yielding an inactive compound to the exclusion of hypochlorite-ions. The average temp. coeff. of the reaction between  $25^\circ$  and  $50^\circ$  is 2.37. The catalyst is not "poisoned" by hydrogen sulphide, potassium cyanide, mercuric chloride, or arsenic trioxide. E. Chirnoaga

represented the reaction by  $-dC/dt = kC^n$ , where  $C$  denotes the concentration of the hypochlorite;  $n$  is a constant; and  $k$  is proportional to the surface area of the catalyst. The order of activity of the oxides is  $\text{Ni} > \text{Co} > \text{Cu} > \text{Fe} > \text{Mn} > \text{Hg}$ . C. R. A. Wright and A. P. Luff found that the reduction with hydrogen begins at about  $110^\circ$ ; but with carbon, at  $260^\circ$ ; and with carbon monoxide, at  $-11^\circ$ . T. Bayley said that the product  $\text{Co}_3\text{O}_5$  is stable at a dull red-heat. H. A. J. Pieters found that mixtures of carbon monoxide and air begin to oxidize at  $40^\circ$  in the presence of cobalt dioxide.

**Percobaltities.**—A. Schwarzenberg observed that when potassium hydroxide is fused in air with cobaltous or cobaltous oxide, or cobaltous carbonate, at a high temp., crystals are formed which can be separated by washing away the excess of alkali. A similar product was obtained by E. Becquerel, and L. Pebal. W. Mayer

obtained it by mixing some chlorate or nitrate with the potassium hydroxide. According to L. Pebal, the black, thin, 6-sided plates have a metallic lustre not unlike a ferruginous mica. They do not react alkaline to litmus. When dried at  $100^{\circ}$ , they do not lose weight when heated to  $200^{\circ}$ . A. Schwarzenberg, and W. Mayer observed that the crystals react alkaline after being strongly heated, and they then give up potassium hydroxide when extracted with water, and cobaltous oxide remains. They lose alkali slowly when treated for a long time with cold water, and rapidly when treated with boiling water. Cold, dil. hydrochloric acid extracts very little alkali, and has no appreciable solvent action, but with conc. hydrochloric acid, the salt dissolves with the evolution of chlorine. The salt is dissolved by other conc. acids; with dil. nitric acid, cobaltous oxide passes into soln. and oxygen is evolved.

L. Pebal assigned to this product a formula  $K_2O.2Co_3O_5$ , but A. Schwarzenberg, and W. Mayer gave  $K_2O.Co_9O_{15}.3H_2O$ , or  $K_2O.3Co_3O_5.3H_2O$ . I. Bellucci and F. Dominici considered that a mistake was made owing to the contamination of the products with silver due to the attack of the silver crucibles by the fused potassium hydroxide, and to the hydrolysis of the compound when it was washed with water. They said that the black, shining, hexagonal plates are really **potassium cobaltous percobaltite**,  $K_2O.CoO.3CoO_2$ ; and added:

The best method of preparing the cobaltous potassium cobaltite in a pure state is to fill a nickel crucible with alternate layers of potassium hydroxide and of either cobaltous carbonate or any oxide of cobalt, and to fuse the mass by gently heating it, afterwards heating more strongly with a Bunsen flame for 3 hours. After cooling in a dry vacuum, the mass is introduced into 12 per cent. potassium hydroxide soln. well cooled with ice. The alkali is renewed several times, the crystals being filtered off by means of a pump, washed repeatedly with alcohol, and dried.

The slender, hexagonal plates so obtained have a steel-grey lustre and they are rapidly hydrolyzed by water. The 6-sided plates of  $Co_3O_5.2H_2O$ , obtained by K. A. Hofmann and H. Hiendlmaier, were probably produced by the hydrolysis of potassium cobaltous percobaltite. W. G. Mixer obtained **sodium percobaltite**,  $Na_2CoO_3$ , by fusing cobalt oxide with sodium dioxide, and he found the heat of formation  $(Co_2O_3.Na_2O)=100.2$  Cals.

G. Rousseau prepared **barium perdicobaltite**,  $BaO.2CoO_2$ , by heating to redness, in an open platinum crucible, a mixture of 15 grms. of hydrated barium chloride or bromide and 5 to 6 grms. of powdered barium oxide, then adding a gram of cobaltic oxide in small quantities at a time. Each addition of the cobaltic oxide is attended by the evolution of oxygen, but the mixture soon enters into quiet fusion. The cold product is lixiviated with water and, finally, acetic acid. The shining, black, hexagonal plates dissolve in conc. hydrochloric acid with evolution of chlorine. The quantity of crystals formed, at first increases, but afterwards diminishes owing to decomposition which is accompanied by slow evolution of oxygen. After prolonged heating, crystals of cobalt oxide are obtained, which are free from barium. If, however, the superficial layer of crystals is continually pressed down into the fused mass beneath, the proportion of barium oxide in the product increases, and the composition of the crystals approximates to **barium percobaltite**,  $BaO.CoO_2$ , or  $Ba(CoO_3)$ . If the fusion is conducted at a higher temp., large, iridescent, black prisms of barium percobaltite are formed and they always contain a small proportion of barium platinate as an impurity. They dissolve in cold hydrochloric acid with evolution of chlorine, and in nitric acid with effervescence. The crystals decompose at a temperature somewhat higher than that at which they are formed, and at an orange-red heat decomposition is very rapid. The temp. of formation of the normal cobaltite lies between  $1000^{\circ}$  and  $1100^{\circ}$ . A somewhat similar phenomenon has already been observed in the case of barium and strontium permanganites, but in these instances the normal manganite was formed at the lower temp., and the acid permanganite at a higher temp. L. E. R. Dufau could not prepare **strontium percobaltite**, or **calcium percobaltite**,

by heating the respective oxides with cobalt in an electric-arc furnace, as in the case of magnesium percobaltite—*vide supra*, cobaltites.

According to J. J. Berzelius, magnesia, or magnesian minerals—free from alumina, or a heavy metal oxide—take on a pale rose-colour when ignited with cobalt nitrate. When ammonia is added to a mixture of neutral magnesium and cobaltous chlorides, a green precipitate is formed. The precipitate does not turn brown during the subsequent washing; it is insoluble in aq. ammonia and ammonium carbonate, but it readily forms a yellow liquid when treated with a soln. of ammonium chloride, and it is again precipitated from the yellow soln. by the addition of potassium hydroxide. The green product becomes greyish-black when ignited. According to L. E. R. Dufau, when an intimate mixture of 150 grms. of cobaltic oxide and 75 grms. of magnesium oxide is heated for 10 mins. in an electric-arc furnace, **magnesium percobaltite**,  $\text{MgO} \cdot \text{CoO}_2$ , or  $\text{Mg}(\text{CoO}_3)$ , is obtained as a very deep, garnet-red, crystalline mass of sp. gr. 5.06 at  $20^\circ$ . Its hardness is between 4 and 5. The cobaltite is dissolved by hydrofluoric acid, by hydrochloric acid with evolution of chlorine, and by nitric and sulphuric acids with evolution of gas, and it is also decomposed and partially dissolved by ammonia. Oxygen is without action on it at a red-heat, but sulphur converts it into cobalt sulphide at a lower temp. Chlorine attacks it with production of cobaltous chloride, which sublimes, and bromine behaves similarly, but iodine seems to have no action. Dry hydrogen fluoride and dry hydrogen chloride also decompose it readily, but fused oxidizing agents have no action on it. A. Serres discussed the magnetic susceptibility, and the magnetic moment. The Curie constant is 4.261, and the Curie temp.,  $164.5^\circ \text{K}$ .

The so-called *Rinman's green*,<sup>2</sup> *zinc green*, or *cobalt green*, obtained by calcining a mixture of cobalt and zinc oxides, may contain some **zinc percobaltite**. Cobaltic oxide,  $\text{Co}_2\text{O}_3$ , is sometimes considered to be **cobaltous percobaltite**,  $\text{Co}(\text{CoO}_3)$ , and the compound,  $\text{Co}_3\text{O}_5$ , to be **cobaltous perdicobaltite**,  $\text{CoO} \cdot 2\text{CoO}_2$ . T. Bayley<sup>3</sup> described the *monohydrate*,  $\text{Co}_3\text{O}_5 \cdot \text{H}_2\text{O}$ ; K. A. Hofmann and H. Hiendlmaier, the *dihydrate*,  $\text{Co}_3\text{O}_5 \cdot 2\text{H}_2\text{O}$ ; and T. Bayley, the *trihydrate*,  $\text{Co}_3\text{O}_5 \cdot 3\text{H}_2\text{O}$ , and the *tetrahydrate*,  $\text{Co}_3\text{O}_5 \cdot 4\text{H}_2\text{O}$ .

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### § 14. Cobalt Fluorides

O. Ruff and E. Ascher<sup>1</sup> observed that the action of fluorine on finely-divided cobalt begins at about 500°, and a mixture of cobaltous and cobaltic fluorides is formed; and if the product is heated in hydrogen at 200° to 300°, the cobaltic fluoride is reduced to **cobaltous fluoride**,  $\text{CoF}_2$ . Other reducing agents act similarly. C. Poulenc prepared cobaltous fluoride by treating cobaltous chloride with gaseous hydrogen fluoride at ordinary temp.; E. Birk and W. Biltz, by heating the tetrahydrate in vacuo over sulphuric acid for 10 hrs. at 150°, and in vacuo over phosphorus pentoxide for 20 hrs. at 300°, finally, heating the product up to the softening temp. of glass. C. Poulenc observed that when cobaltous oxide or hydroxide is treated with hydrogen fluoride at 400° to 500°, it is converted into amorphous cobaltous fluoride, which becomes crystalline if the temp. is raised. C. Poulenc melted anhydrous cobalt chloride with an excess of ammonium fluoride, washing the cold product with alcohol, and heating to redness the resulting ammonium cobalt fluoride in a current of an indifferent gas, say, carbon dioxide. The pulverulent cobalt fluoride so obtained can be converted into a crystalline mass by melting it in a current of hydrogen fluoride. G. L. Clark and H. K. Buckner said that the oxide is formed by this process, but O. Ruff, and E. Birk and W. Biltz verified C. Poulenc's results. K. Jelinek and R. Koop purified the salt by mixing it intimately with ammonium fluoride, and heating the mixture at 400° to 500°, and subliming off the ammonium fluoride in a current of hydrogen fluoride containing a small proportion of hydrogen.

Cobaltous fluoride, according to C. Poulenc, furnishes rose-red, monoclinic prisms; but A. de Schulten said that the crystals are optically positive tetragonal prisms. O. R. Howell, A. Ferrari, and P. P. Ewald and C. Hermann said that the tetragonal crystals have the rutile type of lattice. The X-radiograms of the ruby-red crystals, measured by A. Ferrari, show that the space-lattice is tetragonal and of the rutile type, with the lattice dimensions  $a=4.695$  Å.,  $c=3.193$  Å., and  $a:c=1.0680$ . The vol. of the lattice is  $70.38 \times 10^{-24}$  c.c. W. Zachariasen and V. M. Goldschmidt observed  $a=4.70$  Å., and  $c=3.18$  Å. The shortest distance between the cobalt and fluorine atoms is 2.04 Å. Observations were made by V. M. Goldschmidt, and J. W. Gruner. O. Ruff and E. Ascher calculated from the lattice constants the sp. gr. 4.55; and A. Ferrari, 4.574—C. Poulenc observed 4.43; and E. Birk and W. Biltz, and W. Biltz and E. Rahlfs, 4.460 at 25°/4°, for the sp. gr. E. Birk and W. Biltz calculated 21.74 for the mol. vol.; and G. L. Clark and H. K. Buckner gave 23.0, and showed that there is a 27.5 per cent. contraction in the formation of the compound from its elements. A. Rudat gave for the heats of formation, 160.7 Cals. at 300° to 500°; and for the press.,  $p$ , of the

fluorine at 300°, 400°, 500°, and 600°, respectively,  $3.55 \times 10^{-54}$ ,  $2.45 \times 10^{-45}$ ,  $9.33 \times 10^{-39}$ , and  $2.09 \times 10^{-33}$ . C. Poulenc said that the salt melts between 1100° and 1200°—E. Birk and W. Biltz said over 1000°. K. Jellinek and R. Koop gave for the heat of formation  $(\text{Co}_2\text{F}_2)=160.7$  Cals.; E. Petersen,  $(\text{Co}_2\text{F}_2, \text{Aq.})=125.4$  Cals.; H. von Wartenberg and O. Fitzner,  $(\text{Co}_2\text{F}_2, \text{Aq.})=172.8$  Cals.; E. Petersen found the heat of neutralization of  $\frac{1}{2}\text{Co}(\text{OH})_2$  by  $\text{HFaq.}$  to be 13.245 Cals. G. Beck studied the energy of the molecule. R. A. Houston and co-workers, and G. Denigès measured the absorption spectra of the red aq. soln.; and M. Kimura and M. Takewaki measured the ultra-violet absorption spectrum. N. Costachescu found the mol. conductivity of soln. with a mol of the salt in 100, 500, and 1000 litres to be, respectively, 158.7, 184.0, and 191.9 mhos. The tetrahydrate in aq. soln. is hydrolyzed. G. Gore obtained a black powder on the cathode on electrolyzing a soln. of cobalt fluoride in dil. hydrofluoric acid. O. Liebknecht and A. P. Wills found the mol. magnetic susceptibility of an aq. soln. to be  $10,370 \times 10^{-6}$  mass unit when the sp. susceptibility for water at 18° is  $-0.75 \times 10^{-6}$  mass unit. B. Cabrera and A. Duperier, and P. Henkel and W. Klemm measured the magnetic susceptibility of the anhydrous salt.

C. Poulenc observed that the reduction of cobaltous fluoride by hydrogen begins at a dull red-heat. K. Jellinek and co-workers studied the equilibrium  $\text{CoF}_2 + \text{H}_2 \rightleftharpoons \text{Co} + 2\text{HF}$  approached from the hydrogen side, because of the slow rate of diffusion of hydrogen fluoride through the film of fluoride, first formed on the surface of the metal, when an approach is made from the other side. The equilibrium constants  $K = P^2\text{HF}/p_{\text{H}_2}$  at 300°, 400°, 500°, and 600° are, respectively, 0.00029, 0.01096, 0.1698, and 2.754. O. Ruff found that the salt is stable in cold water; and C. Poulenc showed that the salt is rather more soluble in water than is the nickel salt, and with steam, at a dull red-heat, it is decomposed into hydrogen fluoride and cobaltous oxide. R. H. Carter found that 100 c.c. of a sat. soln. at 25° contained 1.415 grms. of  $\text{CoF}_2$ .

J. L. Gay Lussac and L. J. Thénard evaporated a soln. of cobaltous carbonate in an excess of hydrofluoric acid, and obtained rose-red crystals which, according to J. J. Berzelius, are the *dihydrate*,  $\text{CoF}_2 \cdot 2\text{H}_2\text{O}$ . The dihydrate was also prepared by I. Tananajeff. G. L. Clark and H. K. Buckner reported the *trihydrate*,  $\text{CoF}_2 \cdot 3\text{H}_2\text{O}$ , to be formed in rose-red crystals from a soln. of cobalt carbonate in hydrofluoric acid. Its sp. gr. is 2.583; and it loses all its water of crystallization at 300°. E. Birk and W. Biltz could not confirm the trihydrate; they always obtained the tetrahydrate. N. Costachescu could not prepare the *hexahydrate*,  $\text{CoF}_2 \cdot 6\text{H}_2\text{O}$ , or  $[\text{Co}(\text{H}_2\text{O})_6]\text{F}_2$ , but he obtained the *tetrahydrate*,  $\text{CoF}_2 \cdot 4\text{H}_2\text{O}$ , or  $[\text{Co}(\text{H}_2\text{O})_4]\text{F}_2$ , in two isomeric forms. The  $\alpha$ -form was obtained in large, garnet-red, rhombic octahedra by dissolving freshly-prepared cobalt hydroxide in 40 per cent. hydrofluoric acid, diluting the resulting solution with an equal volume of the acid, and allowing it to crystallize in a vacuum over conc. sulphuric acid. The  $\beta$ -salt is produced when the above solution is precipitated with 96 per cent. alcohol; it forms small, rose-coloured crystals, and is isomorphous with the corresponding nickel salt. The  $\beta$ -salt is more soluble in water (the saturated solution at room temp. is 2.3203 per cent., whilst that of the  $\alpha$ -salt is 2.2328 per cent.) and hydrofluoric acid than the  $\alpha$ -salt; it also loses water more readily, at 60° losing 37.10 per cent.  $\text{H}_2\text{O}$ , whilst the  $\alpha$ -salt loses only 9.35 per cent., and is more reactive than the  $\alpha$ -salt. Both salts give identical solutions in water, as shown by measurement of the electrical conductivity. It is probable that the solids are stereoisomerides, in the  $\alpha$ -form the fluorine atoms being situated at the opposite ends of one of the axes of the octahedron, whilst in the  $\beta$ -form they are at the opposite ends of one of the sides. A. Kurtenacker and co-workers could not dehydrate the tetrahydrate without loss of fluorine. W. Biltz and E. Rahlfs gave 2.192 for the sp. gr. of the  $\beta$ -tetrahydrate at 25°/4°. J. J. Berzelius found that the hydrate dissolves without decomposition in cold water, and in water acidified with hydrofluoric acid, but with hot water, hydrolysis occurs, and a soluble basic salt is formed as

**cobalt oxyfluoride**,  $2\text{CoO} \cdot 2\text{CoF}_2 \cdot \text{H}_2\text{O}$ , and the same product appears when hydrofluoric acid is digested with an excess of cobalt carbonate. N. Costachescu also observed the hydrolysis of the salt in aq. soln., and he gave for the water solubility 1.33 per cent.  $\text{CoF}_2$  at  $20^\circ$ ; R. H. Carter, 1.415 grms.  $\text{CoF}_2$  in 100 c.c. water at  $25^\circ$ , and A. Kurtenacker gave 1.36 grms. of  $\text{CoF}_2$  per 100 c.c. of solution at  $20^\circ$ . The salt is hydrolyzed at higher temperatures.

O. Ruff and E. Ascher said the bromine vapour has no perceptible action on cobaltous fluoride, and similarly with iodine. C. Poulenc said that the anhydrous salt is insoluble in hydrofluoric acid, but O. Ruff and E. Ascher observed that when the soln. in 40 per cent. hydrofluoric acid is evaporated, it furnishes soluble crystals of a hydrate. According to E. Böhm, an excess of hydrofluoric acid acts on cobaltous fluoride forming a soln., which, when evaporated over sulphuric acid, in vacuo, forms an oily liquid from which red, prismatic crystals of **cobalt hydrofluoride**,  $\text{CoF}_2 \cdot 5\text{HF} \cdot 6\text{H}_2\text{O}$ , are deposited. The crystals are isomorphous with the corresponding nickel salt (*q.v.*), and B. Gossner said that the crystals are trigonal, and have a sp. gr. of 2.086. The salt is stable if air be excluded, but it decomposes when heated. It is soluble in water, and dil. acid. N. Costachescu was unable to prepare this or the corresponding nickel salt. Observations on the hydrofluoride were also made by F. Fichter and H. Wolfmann, F. H. Edminster and H. C. Cooper, and E. Birk. A. Kurtenacker and co-workers found the solubility of cobalt fluoride in 3 per cent. hydrofluoric acid to be:

	$20^\circ$	$40^\circ$	$50^\circ$	$80^\circ$	$90^\circ$	$100^\circ$
$\text{CoF}_2$ . . .	3.35	3.48	3.60	3.90	4.61	5.43

The solid phase is  $\text{CoF}_2 \cdot 4\text{H}_2\text{O}$ ; there is no break in the curve. The solubility increases rapidly with increasing concentrations of the acid, for, at  $20^\circ$ , 11.5 per cent. hydrofluoric acid dissolved 5.9 per cent.  $\text{CoF}_2$ ; and 13.5 per cent. hydrofluoric acid, 9.6 per cent.  $\text{CoF}_2$ . C. Poulenc observed that at a dull red-heat, hydrogen chloride forms cobaltous chloride; and at ordinary temp., hydrogen fluoride converts cobalt chloride to fluoride. K. Jellinek and R. Koop gave for the equilibrium constant  $K = [\text{HF}]/[\text{HCl}]$  of the reaction  $\text{CoF}_2 + 2\text{HCl} = \text{CoCl}_2 + 2\text{HF}$ , 0.4 at  $315^\circ$ , and 0.73 at  $532^\circ$ , and for the thermal value of the reaction  $-5.19$  Cals. According to C. Poulenc, conc. hydrochloric acid in the cold dissolves very little fluoride, but the salt is readily soluble in the hot acid. C. Poulenc found that when the fluoride is melted with sulphur, a black product is formed which gives off hydrogen sulphide when treated with hydrochloric acid. O. Ruff and E. Ascher observed that sulphur has very little action, though a trace of cobalt sulphide may be formed; at a red-heat, hydrogen sulphide forms cobalt sulphide; and O. Ruff and E. Ascher observed that the fluoride is darkened by sulphur dioxide at a red-heat. C. Poulenc found that conc. sulphuric acid attacks the salt very slowly in the cold, but rapidly when heated. O. Ruff and E. Ascher observed that when heated in ammonia, the salt is reduced to metal.

G. Gore found that the fluoride is insoluble in liquid ammonia; and when the salt is heated strongly in gaseous ammonia, O. Ruff and E. Ascher observed that metallic cobalt is formed. There is a general tendency for ammoniacal soln. of cobaltous salts to oxidize to cobaltic salts on exposure to air, and to form cobaltamines. The results depend to some extent on the nature of the anion. W. Biltz and co-workers attributed the inertness of the fluoride to a high lattice energy; this steric hindrance, as it is called, enables it to resist the entry of other molecules. They said that the anhydrous chloride does not react with gaseous ammonia nor yet with liquid ammonia at  $-78.5^\circ$ , nor with ammonia under press. at room temp. It is, however, possible to prepare amines in which water is present, and where, it is supposed, the water is associated with the lattice. They were unable to confirm the report of G. L. Clark and H. K. Buckner that **cobaltous triamminofluoride**,  $\text{Co}(\text{NH}_3)_3\text{F}_2$ , is formed as a pink powder, when the hexamine is kept in dry air. It loses all its ammonia at  $40^\circ$ . Nor could they prepare **cobaltous hexamminofluoride**,  $\text{Co}(\text{NH}_3)_6\text{F}_2$ , reported by G. L. Clark and H. K. Buckner to

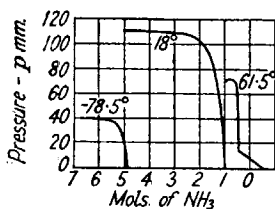


be formed by passing ammonia over dry cobalt fluoride, and allowing the reddish-brown liquid to solidify. Its sp. gr. is 1.744; and it dissolves in water without hydrolysis. The vap. press. of each ammine is said to be 100 mm. at 50°. E. Böhm also showed that the results with fluorides are exceptional, for when a soln. of cobalt hydroxide in hydrofluoric acid is treated with ammonia, and exposed to air for four weeks, a pale yellow crust of ammonium cobaltous fluoride,  $(\text{NH}_4)_2\text{CoF}_4 \cdot 2\text{H}_2\text{O}$ , was formed. W. Biltz and E. Rahlfs cooled in solid carbon dioxide a soln. of 6 grms. of tetrahydrated cobalt fluoride in 25 c.c. of conc. aq. ammonia, and mixed with 40 c.c. of alcohol freed from dissolved air by boiling. Rose-red crystals of **cobaltous aquopentamminofluoride**,  $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]\text{F}_2$ , are formed. The sp. gr. is 1.593 at 25°/4°; the mol. vol. is 125.6; the mol. vol. of the water is 13.6; and the mol. vol. of the ammonia, 18.1. E. Birk and W. Biltz obtained 1.595 at 0°/4° for the sp. gr. The heat of formation is 10.5 Cals. per mol. of ammonia. The vap. press. curves at different temp. are shown in Fig. 75, and:

	-11°	0°	10°	18°	26°
<i>p</i> . . . . .	14.5	32.3	65.5	110.5	175.5 mm.

By reducing the press., **cobaltous aquomonamminofluoride**,  $\text{CoF}_2 \cdot \text{H}_2\text{O} \cdot \text{NH}_3$ , is formed with a sp. gr. 2.471 at 25°/4°; mol. vol., 53.43; mol. vol. of the water, 13.6; and the mol. vol. of the ammonia, 18.1. The vap. press. at 34°, 46.5°, and 61.5° were, respectively, 13.8, 31.5, and 76.4 mm.—Fig. 75. The heat of formation is 12.5 Cals. per mol. of ammonia. There is also formed at 61.5°, **cobaltous aquohexamminofluoride**,  $\text{CoF}_2 \cdot \text{H}_2\text{O} \cdot \frac{1}{2}\text{NH}_3$ . N. Costachescu observed that if cobalt tetrahydrate is dissolved in warm pyridine, and the filtered soln. allowed to crystallize, brick-red, acicular crystals of **cobaltous diaquotetrapyridine fluoride**,  $[\text{Co}(\text{H}_2\text{O})_2\text{Py}_4]\text{F}_2 \cdot \text{H}_2\text{O}$ , are formed. The salt loses pyridine on exposure to air, absorbs some moisture from the atmosphere, and leaves behind tetrahydrated cobalt fluoride. The same salt remains when the soln. of the complex salt in water or alcohol is evaporated. O. Hassel and co-workers found that the compound formed with boron trifluoride, namely, **cobaltous hexamminofluoborate**,  $[\text{Co}(\text{NH}_3)_6](\text{BF}_4)_2$ , has a space lattice with  $a=11.31 \text{ \AA}$ ; and G. B. Naess and O. Hassel, **cobaltous hexamminofluosulphonate**,  $[\text{Co}(\text{NH}_3)_6](\text{SO}_3\text{F})_2$ .

FIG. 75.—The Dissociation Pressures of the Cobalt Aminofluorides.



C. Poulenc observed that cobaltous fluoride is slowly attacked by conc. nitric acid in the cold, but more quickly when heated. Red phosphorus has no perceptible action; and similarly with arsenic and with carbon. C. Poulenc found that the salt is insoluble in benzene, alcohol, and ether. According to O. Ruff and E. Ascher, 12 per cent. acetic acid attacks the salt slowly in the cold, but when heated the salt dissolves freely. N. Costachescu said that cobaltous fluoride is insoluble in pyridine. Crystalline silicon reacts with the fluoride when heated below redness; sodium, magnesium, aluminium, and zinc react vigorously when heated with the fluoride, but no reaction was observed with iron or with copper. When heated with 33 per cent. soda-lye, a blue soln. containing cobalt is formed. C. Poulenc obtained cobaltous oxide and sodium fluoride by melting cobaltous fluoride with sodium carbonate.

**Complex salts of cobaltous fluoride.**—C. Poulenc prepared **ammonium cobalt tetrafluoride**,  $(\text{NH}_4)_2\text{CoF}_4$ , by fusing cobaltous chloride with an excess of ammonium fluoride, and treating the slowly-cooled mass with boiling alcohol. A. Kurtenacker and co-workers studied the equilibrium conditions in the system:  $\text{CoF}_2\text{--NH}_4\text{F--H}_2\text{O}$  at 20°, and found the solubility curve, *S* grms. per 100 grms. of soln., to be:

$\text{NH}_4\text{F}$ . . . . .	2.9	9.7	12.4	18.4	20.8	24.1	34.3
$S(\text{CoF}_2)$ . . . . .	0.34	0.21	0.08	0.02	0.015	0.010	0.009
Solid phase . . . . .	$\text{CoF}_2 \cdot 4\text{H}_2\text{O}$		$2\text{NH}_4\text{F} \cdot \text{CoF}_2 \cdot 2\text{H}_2\text{O}$				

corresponding with the formation of  $(\text{NH}_4)_2\text{CoF}_4 \cdot 2\text{H}_2\text{O}$ . Analogous results were obtained at  $50^\circ$ . C. Poulenc observed that the violet crystalline powder is freely soluble in water, and acids, but insoluble in alcohol. It decomposes at a red-heat, giving off ammonium fluoride, and leaving cobalt fluoride behind. The *dihydrate*,  $(\text{NH}_4)_2\text{CoF}_4 \cdot 2\text{H}_2\text{O}$ , was obtained by H. von Helmolt, by boiling freshly-precipitated cobaltous hydroxide with a neutral soln. of ammonium fluoride; R. Wagner, from a mixed soln. of the component salts; and, as indicated above, by E. Böhm, from a soln. of cobaltous hydroxide in 43 per cent. hydrofluoric acid, saturated with ammonia. J. J. Berzelius said that the salt furnishes a pale red, crystalline mass, slightly soluble in water. E. Böhm said that the pale red crystals are microscopic cubes, and H. von Helmolt, 4-sided tetragonal plates, sparingly soluble in water. E. Böhm found the salt is soluble in dil. acids, and with conc. hydrochloric acid forms cobaltous chloride. C. Poulenc also prepared **potassium cobalt tetrafluoride**,  $\text{K}_2\text{CoF}_4$ , by heating cobalt chloride with potassium hydrofluoride for some hours at  $220^\circ$ , and then at the m.p. The slowly-cooled mass is to be washed with boiling 97 per cent. of alcohol. The garnet-red, quadratic plates have a sp. gr. 3.22; they are sparingly soluble in water, almost insoluble in alcohol, ether, and benzene; freely soluble in hydrofluoric, hydrochloric, and nitric acids; decomposed when heated with sulphuric acid, or with alkali-lye, or alkali carbonate. Ammonia gradually colours the crystals red. The salt is decomposed by heat, with the formation of cobaltic oxide, and the volatilization of potassium fluoride. The salt dissolves in molten alkali silicates, to form a blue glass. J. J. Berzelius prepared a rose-red hydrate from a soln. of the component salts; and, according to R. Wagner, the product is **potassium cobalt trifluoride**,  $\text{KF} \cdot \text{CoF}_2 \cdot \text{H}_2\text{O}$ . A. Kurtenacker and co-workers studied the equilibrium conditions in the system:  $\text{CoF}_2$ - $\text{KF}$ - $\text{H}_2\text{O}$  at  $20^\circ$ , and found the solubility curve, S grms. per 100 grms. of soln., to be:

KF	:	:	:	:	1.2	1.6	2.3	13.8	20.8
S( $\text{CoF}_2$ )	:	:	:	:	0.86	0.18	0.11	0.13	0.005

corresponding with the existence of  $\text{KCoF}_3$ , and similarly at  $50^\circ$ . R. Wagner also prepared crystals of **sodium cobalt trifluoride**,  $\text{NaF} \cdot \text{CoF}_2 \cdot \text{H}_2\text{O}$ , from a mixed soln. of the component salts. The composition of this complex fluoride is not well established. A. Kurtenacker and co-workers found that after 2 months' shaking of the system  $\text{CoF}_2$ - $\text{NaF}$ - $\text{H}_2\text{O}$  at  $20^\circ$  and at  $50^\circ$ , only an incomplete formation of  $\text{CoF} \cdot \text{NaF}$  takes place.

N. N. Ray prepared **cobalt fluoberyllate**,  $\text{CoBeF}_4 \cdot 7\text{H}_2\text{O}$ , by the action of cobalt nitrite on the theoretical quantity of ammonium fluoberyllate. The pale violet crystals of the *heptahydrate* have a sp. gr. 1.867 at  $30^\circ/4^\circ$ , and a mol. vol. 144.6. It loses a mol. of water in air at  $30^\circ$  to  $35^\circ$ , 4 mols. in vacuo over sulphuric acid, and 5 mols. at  $100^\circ$ . R. F. Weinland and O. Köppen evaporated a soln. of aluminium hydroxide and of cobalt hydroxide or carbonate in hydrofluoric acid, at ordinary temp., over lime, and obtained reddish-white crystals of **aluminium cobalt pentafluoride**,  $\text{AlF}_3 \cdot \text{CoF}_2 \cdot 7\text{H}_2\text{O}$ , sparingly soluble in dil. and conc. hydrofluoric acid. E. Rimbach and H. F. C. Kilian obtained **erie cobalt decafluoride**,  $2\text{CeF}_4 \cdot \text{CoF}_2 \cdot 7\text{H}_2\text{O}$ , in pale pink crystals from a mixed soln. of ceric and cobalt hydroxides in hydrofluoric acid. B. Gossner, and P. Engelskirchen prepared **cobaltous fluotitanate**,  $\text{CoTiF}_6 \cdot 6\text{H}_2\text{O}$ ; H. Töpsöe, and B. Gossner, **cobaltous fluostanate**,  $\text{CoSnF}_6 \cdot 6\text{H}_2\text{O}$ ; B. Santesson, and A. Streng, **cobaltous fluocolumbate**,  $\text{Co}_5\text{H}_5\text{C}_3\text{F}_{30} \cdot 28\text{H}_2\text{O}$ , which is insoluble in and decomposed by water. E. Petersen prepared **cobalt fluovanadate**,  $\text{VF}_3 \cdot \text{CoF}_2 \cdot 7\text{H}_2\text{O}$ , by allowing a mixed soln. of the component salts to evaporate slowly, or to stand for some time; and A. Piccini and G. Georgis obtained it by the prolonged electrolysis of a soln. of a vanadic oxide and cobalt carbonate in hydrofluoric acid. The crystals are dark green when moist, brownish-green when dry; they are probably monoclinic, and are stable at  $100^\circ$ , but lose water at  $170^\circ$ . A. Piccini and G. Georgis prepared **cobalt fluoxyvanadate**,  $\text{VOF}_2 \cdot \text{CoF}_2 \cdot 7\text{H}_2\text{O}$ , by reducing electrolytically a soln. of

vanadic acid and a little less than the required mol. proportion of cobalt carbonate in hydrofluoric acid. When the soln. is intensely blue, it is filtered and evaporated. The bottle-green prisms have a violet reflex; and they begin to lose water at  $80^{\circ}$ , becoming anhydrous at  $160^{\circ}$ . E. Petersen prepared dark green crystals of **chromic cobalt pentafluoride**,  $\text{CrF}_3 \cdot \text{CoF}_2 \cdot 7\text{H}_2\text{O}$ , by allowing a mixed soln. of the component salts to stand for some time, or to evaporate very slowly. The dark green crystals are isomorphous with the corresponding vanadium salt. They are stable at  $100^{\circ}$ , but lose water at  $200^{\circ}$ . M. Delafontaine obtained crystals of **cobalt oxyfluomolybdate**,  $\text{MoO}_2\text{F}_2 \cdot \text{CoF}_2 \cdot 6\text{H}_2\text{O}$ , by evaporating a soln. of eq. proportions of cobalt hydroxide or carbonate, and molybdic oxide in hydrofluoric acid. According to B. Gossner, the dark green, hexagonal crystals are isomorphous with the corresponding fluosilicate—**6**. 40, 56; they are stable in dry air, but they decompose when heated. O. T. Christensen prepared **manganic cobaltous pentafluoride**,  $\text{MnF}_3 \cdot \text{CoF}_2 \cdot 4\text{H}_2\text{O}$ , soluble in water; and R. F. Weinland and O. Köppen prepared **ferric cobaltous pentafluoride**,  $\text{FeCl}_3 \cdot \text{CoCl}_2 \cdot 7\text{H}_2\text{O}$ , in rose-red crystals, by evaporating a mixed soln. of the component salts in dil. hydrofluoric acid over calcium chloride at ordinary temp.

**Cobaltic fluoride.**—O. Ruff, and O. Ruff and E. Ascher prepared the anhydrous trifluoride by the action of fluorine on cobalt dichloride in a quartz tube at  $150^{\circ}$ . F. Fichter and H. Wolfmann, and N. C. Jones found that some cobaltic fluoride,  $\text{CoF}_3$ , is formed in aq. soln. when a soln. of cobaltous fluoride is treated with fluorine. According to G. A. Barbieri and F. Calzolari, when a sat. soln. of cobaltous fluoride, in 40 per cent. hydrofluoric acid, is electrolyzed in a platinum dish as anode, and a platinum wire as cathode, with anodic current density of 1 ampere per sq. dm., cobaltic fluoride,  $\text{CoF}_3 \cdot n\text{H}_2\text{O}$ , is deposited as a green powder which does not re-dissolve when the current is cut off. According to E. Birk, G. A. Barbieri and F. Calzolari, the salt is the *hemiheptahydrate*,  $2\text{CoF}_3 \cdot 7\text{H}_2\text{O}$ , and hence its formula may be:  $\text{Fe}_2\text{F}_6 \cdot 7\text{H}_2\text{O}$ , by analogy with  $\text{Cr}_2\text{F}_6 \cdot 7\text{H}_2\text{O}$ ,  $\text{Fe}_2\text{F}_6 \cdot 9\text{H}_2\text{O}$ , and  $\text{Al}_2\text{F}_6$ ; or it may be written  $[\text{CoF}_3(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$ , analogous with the corresponding hydrates of ferric, chromic, and aluminium fluorides. The X-radiogram shows that the hydrate belongs to the bimolecular type characteristic of  $\text{Cr}_2\text{F}_6 \cdot 7\text{H}_2\text{O}$ . O. Ruff and E. Ascher found that the anhydrous fluoride forms light brown, hygroscopic crystals belonging to the hexagonal system. The lattice dimensions are  $a=7.64 \text{ \AA.}$ ,  $c=3.66 \text{ \AA.}$ ;  $a:c=1:0.508$ ; the vol. of the lattice is  $185 \times 10^{-24} \text{ c.c.}$ ; and there are 4 mols. per unit cell. F. Ebert found that the X-radiograms of the crystals have the parameter, if rhombohedral,  $a=3.664$ , and  $\alpha=87^{\circ} 20'$ ; and if hexagonal,  $a=5.061 \text{ \AA.}$ , and  $c=6.63$ , and  $a:c=1:1.31$ . The vol. of the elementary rhombohedral cell is  $49.05 \times 10^{-24} \text{ c.c.}$  per mol. The shortest distance between the cobalt and fluorine atoms is  $2.02 \text{ \AA.}$  The calculated sp. gr. is  $3.89$ —O. Ruff and E. Ascher obtained  $4.14$ —and the observed value is  $3.88$ . J. A. A. Ketelaar found that the crystals are hexagonal, and isomorphous with those of iron, aluminium, palladium, and rhodium. W. Nowacki studied the lattice structure. The sp. gr. is  $3.88$ , and that calculated from the X-radiogram is  $4.14$ . E. Birk found the sp. gr. of the hemiheptahydrate to be  $2.314$  at  $25^{\circ}/4^{\circ}$ ; and the calculated mol. vol.,  $154.7$ . According to O. Ruff and E. Ascher, when the trifluoride is heated in an inert gas, it forms cobaltous fluoride at  $350^{\circ}$ . K. Jellinek and R. Koop found for the partial press. of the fluorine in cobaltic fluoride,  $3.8 \times 10^{-65}$  at  $197^{\circ}$ ;  $3.5 \times 10^{-57}$  at  $254^{\circ}$ ; and  $1.3 \times 10^{-49}$  at  $322^{\circ}$ . The heat of formation of the anhydrous fluoride is about 240 Cals. K. Jellinek and R. Koop gave for  $(2\text{CoF}_2, \text{F}_2)=159.2 \text{ Cals.}$ ; for  $(\text{Co}, \text{F}_2)=160.7 \text{ Cals.}$ ; and for  $(\text{Co}, 1\frac{1}{2}\text{F}_2)=240.3 \text{ Cals.}$  P. Henkel and W. Klemm studied the magnetic properties.

According to O. Ruff and E. Ascher, cobaltic fluoride in hydrogen at  $200^{\circ}$  and  $250^{\circ}$  is reduced to cobaltous fluoride, and the reduction is complete at a red-heat. K. Jellinek and R. Koop found for the equilibrium constant  $K=P_{\text{HF}}^2/P_{\text{H}_2}$ , of the reaction:  $2\text{CoF}_3 + \text{H}_2 \rightleftharpoons 2\text{CoF}_2 + 2\text{HF}$ ,  $K=0.0001622$  at  $197^{\circ}$ ;  $0.00490$  at  $254^{\circ}$ ; and  $0.1698$  at  $322^{\circ}$ ; or,  $P_{\text{HF}}=1.27, 6.81, \text{ and } 33.75$ , respectively. According

to O. Ruff and E. Ascher, when cobaltic fluoride is heated in air, it becomes rose-coloured at  $250^{\circ}$  to  $300^{\circ}$ , forming cobaltous fluoride or a basic salt, and it is converted into the black oxide at  $450^{\circ}$  to  $500^{\circ}$ . G. A. Barbieri and F. Calzolari said that the hydrated salt remains unchanged for several days in a desiccator, but in air it gradually becomes grey and then red in colour. When the anhydrous salt is treated with water, O. Ruff and E. Ascher found that oxygen is evolved, with the formation of a red soln. and black precipitate; water vapour rapidly darkens the colour of the salt at ordinary temp. G. A. Barbieri and F. Calzolari observed that the addition of a few drops of water to the hydrate blackens the salt, owing to the formation of cobaltic hydroxide; hydrogen dioxide reduces the sulphuric acid soln. of the hydrate immediately.

O. Ruff and E. Ascher found that bromine vapour above  $100^{\circ}$  reacts with the anhydrous salt, forming a bromiferous intermediate product, and cobaltous fluoride as end-product; when heated with iodine, there is a vigorous reaction, and cobaltous fluoride being formed. When the trifluoride is heated in hydrogen chloride, cobaltous chloride is formed. Forty per cent. hydrofluoric acid acts on the anhydrous salt, oxygen is evolved, and the red soln. becomes green, a residue—possibly the hydrated salt—remains. With conc. hydrochloric acid, chlorine is evolved, and a soln. of cobaltous chloride is formed.

According to J. Fischer and W. Jaenckner, there is a detonation when a mixture of sulphur and the anhydrous trifluoride is warmed, sulphur tetrafluoride and cobaltous fluoride is formed. O. Ruff and E. Ascher observed that with hydrogen sulphide at ordinary temp., cobaltous fluoride is formed, with evolution of heat, and cobalt sulphide is produced when the mixture is heated. When the trifluoride is heated to  $200^{\circ}$  in contact with sulphur dioxide, cobaltous fluoride is formed. When the trifluoride is heated with conc. sulphuric acid, oxygen and hydrogen fluoride are given off, and cobaltous sulphate remains in soln. G. A. Barbieri and F. Calzolari observed that the hydrate forms a brown soln. with sulphuric acid, which, when diluted, turns green.

O. Ruff and E. Ascher found that when heated below  $100^{\circ}$  in ammonia, the mixture reacts violently, forming cobaltous fluoride and a white sublimate of ammonium fluoride. E. Birk observed that the hydrated trifluoride takes up ammonia at  $70^{\circ}$  to  $80^{\circ}$ , with the loss of water, and the formation of luteo- and purpureo-fluorides. G. A. Barbieri and F. Calzolari found that the sulphuric acid soln. of the hydrated salt turns red when gently heated, or when treated with a reducing agent like a nitrite, hydroxylamine, hydrazine, or hydrogen dioxide. O. Ruff and E. Ascher observed that conc. nitric acid in the cold forms a dark green soln. which, when heated, gives off oxygen and forms a red soln. of cobaltous nitrate. Red phosphorus reacts when warmed with the anhydrous fluoride, and cobaltous fluoride is produced; similarly with arsenic.

O. Ruff and E. Ascher found that carbon also reacts when warmed with the trifluoride, forming cobaltous fluoride. The anhydrous fluoride is insoluble in benzene, alcohol, and ether. When alcohol is added to the brown sulphuric acid soln. of the hydrate, G. A. Barbieri and F. Calzolari observed that its colour changes to red. O. Ruff and E. Ascher found that 12 per cent. acetic acid in the cold forms a brown soln. which, when warmed, gives off oxygen with the separation of a black precipitate. The trifluoride reacts vigorously when it is heated with crystalline silicon, and cobaltous fluoride is formed.

According to O. Ruff and E. Ascher, the trifluoride reacts vigorously when heated with sodium, magnesium, aluminium, zinc, copper, iron, and cobalt—in the latter case,  $2\text{CoF}_3 + \text{Co} = 3\text{CoF}_2$ . A 40 per cent. soln. of sodium hydroxide reacts with the trifluoride, giving off oxygen in the cold, and depositing a black precipitate. When the trifluoride is melted with sodium carbonate, cobaltous oxide and sodium fluoride are produced.

E. Böhm prepared the normal **cobaltic hexamminofluoride**,  $[\text{Co}(\text{NH}_3)_6]\text{F}_3$ , along with the fluochloride, by treating the hexamminochloride with hydrofluoric

acid. The yellow, prismatic crystals are sparingly soluble in cold water, and almost insoluble in acids. H. Drawe gave 2.072 for the sp. gr., and 80.65 for the mol. vol. A. Miolati and G. Rossi obtained **cobaltic hexamminohydrofluoride**,  $[\text{Co}(\text{NH}_3)_6]\text{F}_6\text{H}_3$ , or  $[\text{Co}(\text{NH}_3)_6]\text{F}_3 \cdot 3\text{HF}$ , by treating cobaltic hexamminocarbonate with an excess of hydrofluoric acid, and silver fluoride. The orange-yellow crystals lose 3 mols. of hydrogen fluoride at  $105^\circ$ . The salt is freely soluble in water, and the eq. conductivity,  $\lambda$  soln. of an eq. of the salt,  $\frac{1}{3}[\text{Co}(\text{NH}_3)_6]\text{F}_6\text{H}_3$ , in  $v$  litres of water at  $25^\circ$ , is:

$v$ :	:	32	64	128	256	512	1024
$\lambda$ :	:	110.4	123.4	142.0	167.3	205.1	263.6

W. Biltz, E. Birk, and E. Birk and W. Biltz prepared **cobaltic hexamminohydrofluoride**,  $[\text{Co}(\text{NH}_3)_6]\text{F}_3 \cdot 6\text{HF}$ , by precipitation from an aq. soln. of the neutral fluoride and 50 per cent. hydrofluoric acid, and subsequent crystallization from 0.1 per cent. hydrofluoric acid. The sp. gr. of the crystals is 1.938 at  $25^\circ/4^\circ$ , and the mol. vol. is 174.5. A litre of hot 0.1 per cent. hydrofluoric acid dissolves about 1.5 grms. of the salt. H. Seibt obtained yellow **cobaltic trisethylenediaminofluoride**,  $[\text{Co en}_3]\text{F}_3$ , by treating a soln. of the bromide with silver fluoride. J. Angerstein studied the absorption spectra of the soln.

A. Hiendlmayr, W. Biltz, and E. Birk and W. Biltz prepared **cobaltic aquopentamminofluoride**,  $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]\text{F}_3$ , by neutralizing the aq. soln. of the hydroxide with 40 per cent. hydrofluoric acid, cooled by ice. The wine-red crystals are very soluble in water; their sp. gr. is 1.748 at  $25^\circ/4^\circ$ , and the mol. vol. is 125.4. If an excess of hydrofluoric acid is employed, **cobaltic aquopentamminotrifluorohexahydrofluoride**,  $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]\text{F}_3 \cdot 6\text{HF}$ , is formed. The sp. gr. is 1.976 at  $25^\circ/4^\circ$ , and the mol. vol. 171.7. C. S. Borzekowsky prepared the dextro- and laevo-forms of **cobaltic hydroxylaminebisethylenediamineamminohydroxide**,  $[\text{Co}(\text{NH}_3)(\text{NH}_2\text{OH en}_2)(\text{OH})_3]$ .

A. Hiendlmayr, and E. Birk prepared **cobaltic fluopentamminofluoride**,  $[\text{Co}(\text{NH}_3)_5\text{F}]\text{F}_2$ , by the action of ammonia on hemiheptahydrated cobaltous fluoride at  $70^\circ$  to  $80^\circ$ ; and a part of the salt—possibly hexamminofluoride—dissolves in ice-water, forming a yellow liquid, the remainder—the fluopentamminofluoride—forms a red soln. with warm water acidified with hydrofluoric acid.

H. Seibt prepared **cobaltic cis-fluobisethylenediamineamminofluoride**,  $[\text{Co}(\text{NH}_3)_2\text{en}_2\text{F}]\text{F}_2$ , as a red, crystalline powder by shaking an aq. soln. of cobaltic cis-aquobisethylenediamineamminobromide, with an excess of freshly-precipitated silver oxide, adding 40 per cent. hydrofluoric acid, and evaporating to dryness. M. L. Ernsberger and W. R. Brode studied the absorption spectrum. H. Seibt obtained the corresponding **cobaltic trans-aquobisethylenediamineamminofluoride** by similarly treating trans-aquobisethylenediamineamminobromide. H. Seibt prepared **cobaltic trans-difluobisethylenediaminefluoride**,  $[\text{Co en}_2\text{F}_2]\text{F}$ , in dark green crystals, by the action of hydrofluoric acid on carbonatobisethylenediaminehydroxide.

A. Miolati and G. Rossi also prepared a series of complex salts, thus: a soln. of boric acid in an excess of hydrofluoric acid converts cobaltic hexamminocarbonate into **cobaltic boron hexamminofluoride**,  $[\text{Co}(\text{NH}_3)_6]\text{F}_3 \cdot 3\text{BF}_3 \cdot \text{HF}$ , which appears as a yellow, crystalline powder. By replacing the boric acid with fluosilicic acid, **cobaltic silicon hexamminofluoride**,  $[\text{Co}(\text{NH}_3)_6]\text{F}_3 \cdot 2\text{SiF}_4$ , is formed as a yellow, crystalline powder; with titanilic acid, **cobaltic titanium hexamminofluoride**,  $[\text{Co}(\text{NH}_3)_6]\text{F}_3 \cdot \text{TiF}_4 \cdot 2\text{HF}$ , is formed as a yellow, crystalline powder; with ammonium metavanadate, **cobaltic vanadyl hexamminofluoride**,  $[\text{Co}(\text{NH}_3)_6]\text{F}_3 \cdot 5\text{VO}_2\text{F}_2 \cdot 7\text{HF}$ ; with molybdenum dioxyfluoride, **cobaltic molybdenyl hexamminofluoride**,  $[\text{Co}(\text{NH}_3)_6]\text{F}_3 \cdot 2\text{MoO}_2\text{F}_2$ , as a yellow, crystalline powder; with tungsten dioxydifluoride, **cobaltic tungstyl hexamminofluoride**,  $[\text{Co}(\text{NH}_3)_6]\text{F}_3 \cdot 2\text{WO}_2\text{F}_2$ , as a yellow, crystalline powder; and with ammonium uranyl fluoride, **cobaltic uranyl hexamminofluoride**,  $[\text{Co}(\text{NH}_3)_6]\text{F}_3 \cdot \text{UO}_2\text{F}_2$ , as a yellow powder.

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## § 15. Cobaltous Chloride

H. Davy<sup>1</sup> obtained cobaltous chloride,  $\text{CoCl}_2$ , by heating finely-divided cobalt in a current of chlorine, and H. Rose observed that finely-divided cobalt takes fire in a current of chlorine, producing blue, crystalline scales of the anhydrous chloride. When the chloride is strongly heated in a retort, or in a current of chlorine, cobalt chloride sublimes to form crystalline spangles which are slippery to the touch. G. C. Winkelblech obtained the chloride in this manner. According to R. Weber, cobalt oxide is not attacked by chlorine so readily as is the case with nickel oxide;

and R. Wasmuth observed that at  $500^{\circ}$ , about half the oxide is converted into chloride. A. Michael and A. Murphy obtained the chloride by the action of carbon tetrachloride on cobalt oxide in a sealed tube at  $100^{\circ}$ . H. Quantin also used carbon tetrachloride vapour, or a mixture of carbon dioxide and chlorine at a red-heat. A. Camboulives found that the reaction with carbon tetrachloride begins at  $550^{\circ}$ . F. Bourion obtained the chloride by heating the oxide in the vapour of sulphur monochloride. The reaction begins at about  $250^{\circ}$ , and the temp. was gradually raised to  $500^{\circ}$  during 3 hrs., and the product cooled in hydrogen chloride. The product is not pure. A. Hantzsch heated cobalt hydroxide in the vapour of acetyl or benzoyl chloride and obtained a quantitative yield of cobalt chloride. G. N. Wyrouboff obtained the anhydrous salt by dehydrating the hydrate at  $135^{\circ}$  to  $140^{\circ}$ ; J. Bersch, and W. Biltz and B. Fetkenheuer recommended a temp. exceeding  $140^{\circ}$ ; and G. L. Clark and co-workers,  $160^{\circ}$  to  $170^{\circ}$ . A. L. Potilitzin found that the salt dried at  $110^{\circ}$  to  $120^{\circ}$  for 13 hrs. is not completely soluble in water, and to avoid the formation of insoluble basic salt, he recommended drying the hydrate first over sulphuric acid, then heating it at  $100^{\circ}$ , and finally gently warming the product in a current of hydrogen chloride mixed with chlorine. G. P. Baxter and co-workers obtained the chloride of a high degree of purity by heating the hydrate in quartz vessels in a current of hydrogen chloride. F. W. O. de Coninck obtained the anhydrous salt by heating one of the hydrates with glycol under pressure. W. G. Leison, F. Rose, H. Copaux, and W. Biltz prepared the salt by heating cobaltic chloropentamminochloride. G. P. Baxter and F. B. Coffin, and T. W. Richards and G. P. Baxter observed that the product is of a high degree of purity if the ammine be heated in a quartz vessel, and the ammonium chloride be expelled by heating the product in a current of nitrogen and hydrogen chloride.

According to R. Engel, the *monohydrate*,  $\text{CoCl}_2 \cdot \text{H}_2\text{O}$ , is formed when a soln. of the hexahydrate is evaporated to dryness at  $100^{\circ}$ . A. Ditte obtained it by passing hydrogen chloride through a soln. of the hexahydrate in hydrochloric acid at  $35^{\circ}$ ; and G. N. Wyrouboff obtained it by warming the hexahydrate at  $80^{\circ}$  to  $90^{\circ}$ . A. Hantzsch and F. Schlegel said  $90^{\circ}$ , and A. L. Potilitzin,  $100^{\circ}$ . A. L. Potilitzin observed that when the dihydrate is heated to  $100^{\circ}$ , dark violet spots appear on the rose-red hydrate in about 1 hour, they do not disappear on cooling, and they increase in size when the hydrate is kept at  $100^{\circ}$ ; until, in  $4\frac{1}{2}$  hrs., all is converted into violet monohydrate. The product obtained by dehydrating the higher hydrates is said to be amorphous, and A. L. Potilitzin found that needle-like crystals can be produced by heating a higher hydrate dissolved in absolute alcohol at  $90^{\circ}$  to  $95^{\circ}$ , on an air-bath, until all the alcohol is removed. A. Ditte said that a *hemitrihydrate*,  $\text{CoCl}_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ , is produced when hydrogen chloride is passed slowly through a soln. of cobalt chloride saturated at  $12^{\circ}$ ; but A. Hantzsch could not confirm the existence of these salts by observations on the dehydration of the higher hydrate. The *dihydrate*,  $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ , was prepared by J. Bersch, and E. J. Mills by heating a higher hydrate; by drying the higher hydrate in a desiccator over sulphuric acid; or, according to P. Sabatier, by drying the higher hydrate in vacuo—A. L. Potilitzin added that 4 or 5 days are needed for the operation, but H. Lescœur found that about 24 hrs. are needed if the salt be kept over conc. sulphuric acid at  $30^{\circ}$  to  $40^{\circ}$ ; and A. L. Potilitzin found that only 4 hrs. are necessary at  $45^{\circ}$  to  $52^{\circ}$ . A. Neuhaus, and G. L. Clark and co-workers recommended keeping the hexahydrate over conc. sulphuric acid for 36 hrs. at  $50^{\circ}$ . According to A. Etard, the dihydrate is the solid phase in sat. aq. soln. at temp. exceeding  $50^{\circ}$ . A. Hantzsch reported a blue, unstable form of the dihydrate analogous with a blue, unstable cobaltous bispyridinoclchloride,  $\text{CoCl}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$ . J. Bersch reported the *tetrahydrate*,  $\text{CoCl}_2 \cdot 4\text{H}_2\text{O}$ , to be formed by heating the hexahydrate at  $116^{\circ}$ . It was also mentioned by A. Neuhaus, and F. W. O. de Coninck; and H. Benrath found that the monoclinic crystals are stable between  $46^{\circ}$  and  $48^{\circ}$  approximately. A. Hantzsch's works on the dehydration, and H. Lescœur's observations on the vapour press. of the hydrates of cobalt chloride gave no evidence of the *existence*

of the tetrahydrate. I. H. Derby and V. Yngve, and G. L. Clark and co-workers also failed to prepare the tetrahydrate. W. Stortenbeker observed that the tetrahydrate forms solid soln. with the tetrahydrate of manganous chloride, and that there are two forms,  $\alpha$ -tetrahydrate and  $\beta$ -tetrahydrate. A. Benrath's observations on the solubility of cobaltous chloride are summarized in Fig. 76. The diagram shows the equilibrium conditions of the three hydrates.

The aq. soln. is obtained by dissolving one of the hydrates in water. According to J. L. Proust, C. F. Bucholz, and L. R. von Fellenberg, when the sublimed, blue chloride is exposed to air, it acquires a red colour, and it then readily dissolves in water, but if the salt has not been previously exposed to air, it requires 12 hrs. or more to get it into soln. The aq. soln. of cobalt chloride is readily formed by dissolving the oxide, hydroxide or carbonate in hydrochloric acid, or by dissolving the metal in hydrochloric acid, or in aqua regia. If the aq. soln. be evaporated for crystallization, the *hexahydrate*,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , is formed. The salt was prepared by H. Copaux, R. Engel, L. R. von Fellenberg, F. Feigl and co-workers, H. J. Kapulitzas, and A. L. Potilitzin. E. J. Mills obtained the aq. soln. by repeatedly digesting cobaltic chloropentamminodichloride with hydrochloric acid. The *octohydrate*,  $\text{CoCl}_2 \cdot 8\text{H}_2\text{O}$ , mentioned by C. F. Rammelsberg, and H. J. Brooke, could not be prepared by J. C. G. de Marignac, and no one else has recognized its existence. The product is the hexahydrate.

**Physical properties of cobalt chloride.**—According to J. L. Proust, the **colour** of the sublimed chloride is flax-flower blue, according to C. F. Bucholz, blue; and according to L. R. von Fellenberg, bluish-green. R. Engel said that the crystals of the anhydrous salt are pale blue, and that also is the colour of the loosely-coherent mass obtained by dehydration. F. G. Donnan and H. Bassett observed that the colour of the anhydrous salt is pale blue at ordinary temp., and reddish-violet at the b.p. of liquid air. The monohydrate was also stated by R. Engel, A. Ditte, and A. L. Potilitzin, etc., to be violet or bluish-violet; the hemitrihydrate, according to A. Ditte, is also bluish-violet; the dihydrate, according to J. Bersch, is deep violet-blue; if not completely dehydrated, the colour is rose-red tinged with violet. J. Bersch, and A. Neuhaus said that the tetrahydrate is peach-red, or red; W. Stortenbeker studied the solid soln. of cobalt and manganous chlorides, and from the results inferred the existence of isomeric forms,  $\alpha$ -tetrahydrate and  $\beta$ -tetrahydrate, and the colours deduced from their solid soln. are, respectively, violet, and violet-red. According to A. Neuhaus, and O. Mügge, the carmine-red, or red crystals of the hexahydrate are pleochroic, having  $\alpha$ , ultramarine to prussian-blue;  $\beta$ , a pale carmine-red; and  $\gamma$ , a clear carmine-red.

Observations on the changes in the colour of soln. of cobaltous chloride were made by J. Hellot, P. J. Macquer, and J. L. Proust. According to J. Bersch, and A. Vogel, the carmine-red or pink aq. soln. of cobalt chloride turn violet-blue when heated, and this is the case even with very dilute soln. The changes in colour of the red soln. on heating correspond with the changes in colour in passing from the hexahydrate to the anhydrous chloride, and, roughly, with the zones of stability of the different hydrates on the solubility curves. The aq. soln. also turns blue when mixed with alcohol, or with conc. hydrochloric or sulphuric acid, and this the more readily, the lower the temp. The red colour can be restored by diluting the soln. with water, and in some cases by cooling the blue liquid. The more dilute soln., if it contains free acid, also turns blue when it is concentrated by heat, or by standing over sulphuric acid under reduced pressure. The blue soln. in alcohol on dilution with water, becomes first violet and then red, and it also becomes red when cooled much below  $0^\circ$ . According to R. Engel, and J. Kallir, the red, aq.

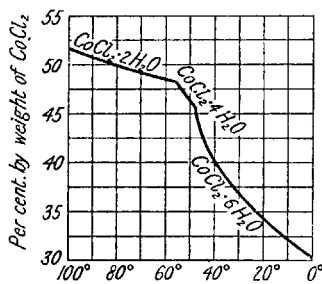


Fig. 76.—The Solubility of the Cobaltous Chloride.



soln. also turns blue when it is treated with the chlorides of zinc, tin (ous), mercury (ic), and lithium. F. W. O. de Coninck also found that the red soln. becomes violet in sunlight. For the application of the facts to the preparation of an invisible or sympathetic ink, *vide supra*, uses of cobalt.

One of the earliest guesses made to explain these colour-changes was to assume that the red colour is due to the existence of the hexahydrate in soln., and that the blue colour is due to the formation of a lower hydrate. The *hydration hypothesis* was discussed by C. H. L. von Babo, A. Benrath, M. Berthelot, A. R. Brown, G. Chancel, G. Charpy, F. Clowes, A. Étard, J. H. Gladstone, R. Godeffroy, W. N. Hartley, N. S. Kurnakoff, B. E. Moore, A. L. Potilitzin, W. J. Russell, W. J. Russell and W. J. Orsman, H. Schiff, C. R. C. Tichborne, M. S. Wreowsky, and G. N. Wyruboff. The hypothesis, though plausible, does not explain all the phenomena, as, for example, the different effects produced by anhydrous calcium and zinc chlorides. Accordingly, R. Engel elaborated the *molecular compound hypothesis*; he assumed that the various colours are produced by the presence of double salts in soln. He supposed that when the aq. soln. is heated, the salt is partially hydrolyzed, the liberated hydrochloric acid then unites with the unchanged cobalt chloride to form a blue chlorohydrate—*vide infra*. The change from blue to red on adding zinc or mercuric chloride, is attributed to the formation of chlorohydrates by these salts in preference to the chlorohydrate of the cobalt salt, whereas the blue coloration produced by calcium, and lithium chlorides, is due to the formation of double salts—e.g., A. Chassevant's  $\text{CoCl}_2 \cdot \text{LiCl} \cdot 3\text{H}_2\text{O}$ . The subject was discussed by H. le Chatelier, G. N. Wyruboff, and J. Kallir. W. Hardt, as a result of his study of the spectra and electrical conductivities of alcoholic soln., concluded that electrically neutral molecules of cobalt chloride are not present, but rather does the salt form with alcohol *Molekülkomplexen*. The hypothesis fits in with some of the facts, but it has to be supported by too many unproved subsidiary hypotheses to be satisfactory.

J. Bersch postulated an *isomeric hypothesis*, for he said that there is a change from red hexahydrate to blue hexahydrate between  $30^\circ$  and  $35^\circ$ , and he thus attributed the different colours to the presence of different isomers. Neither A. L. Potilitzin, nor H. Lesceur could confirm this conclusion, and they showed that J. Bersch was probably misled by the hexahydrate, at its transition point, melting in its water of crystallization and producing a small proportion of a blue, saturated soln. I. Rohde and E. Vogt found that the absorption spectra of soln. of cobaltous chloride in pyridine, shifts from the red to the blue between about  $10^\circ$  to  $50^\circ$ . The absorption spectrum is not due to a continuous change in the absorption curve for one molecular species, but is due to the displacement of equilibrium between two kinds of molecules as the temp. changes. There is a unimolecular reaction,  $\text{Co}_{\text{red}} \rightleftharpoons \text{Co}_{\text{blue}}$ , which has a thermal value of 11.7 Cals. In a soln. which is blue at  $50^\circ$ , there is present 90 per cent. of  $\text{Co}_{\text{red}}$ , and at  $90^\circ$ , the  $\text{Co}_{\text{red}}$  amounts to 50 per cent. A. Hantzsch and co-workers, and F. Schlegel postulated the existence of red and blue, what he called pseudo-salts, e.g.,  $[\text{Co}(\text{H}_2\text{O})_n]\text{Cl}_2$ , and blue true-salts, e.g.,  $\text{CoCl}_2 \cdot n\text{H}_2\text{O}$ , and suggested that the solid, purple dihydrate gives a blue form in soln. which is unstable in the solid state. He assumed that hydration is the primary cause of the variations of colour. The compound  $\text{CoCl}_2(\text{H}_2\text{O})_4$  is red;  $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_2$  is rose-red; and the solid  $\text{CoCl}_2(\text{H}_2\text{O})_2$  is blue or violet, since it is supposed to exist in *cis* or *trans* modifications:



W. Ostwald suggested an explanation based on the *ionic hypothesis*. He said:

The colours of salt soln. are essentially the colours of the parts of molecules or ions contained therein, and all salt soln. which contain a certain ion, must exhibit the characteristic colour of that ion. Should the expected colour not appear, we may conclude that the corresponding ion is absent. The red colour of dil. soln. of cobalt salts, for instance,

indicates the presence of cobalt ions. The sulphate, nitrate, chloride, etc., have the same colour in soln., and the colour is independent of the nature of the negative ion. If one of these soln. be boiled with an excess of potassium cyanide, it is decolorized, and the colourless soln. no longer shows the reactions of cobalt. The compound potassium cobaltcyanide,  $K_3CoCy_6$ , has been formed, and free cobalt ions are no longer present. The green colour of a soln. of a nickel salt is changed under the same conditions, to yellow, which shows that the nickel ions have entered into combination. If the foregoing statement is correct, the intensity of the coloration of those salts whose ions are coloured must be proportional to the quantity of those ions, supposing that the part of the salt which is not separated into ions is itself colourless. . . . Special relations are observed when the non-ionized salt is itself coloured. For instance, anhydrous cupric chloride, or a soln. of this salt in inert solvents, where it is not separated into ions, is coloured intensely yellow. Therefore a soln. of this salt, which contains many free ions of copper and chlorine, but also a certain amount of non-ionized molecules of cupric chloride, will show the colour which results from mixing the blue of the copper ions with the yellow of cupric chloride. Agreeably with this conclusion, it is found that very dil. soln. of cupric chloride—which contain but little non-ionized salt—are blue, like soln. of other cupric salts, but the more concentrated the soln. become and therefore the greater becomes the number of non-ionized molecules, the more does the colour incline to green. The addition of hydrochloric acid, or the raising of the temp., acts in the same way as increasing the concentration; in both cases, the number of copper ions decreases, and the number of undecomposed molecules of cupric chloride increases.

The hypothesis was favoured by W. C. D. Whetham. This hypothesis requires that the blue colour produced by a rise in temp. is attended by a marked decrease in ionization, and that the addition of other chlorides makes the soln. blue by decreasing the ionization of cobalt chloride. This is not in accord with the observations of R. Salvadori, for F. G. Donnan and H. Bassett showed that they indicate that cobalt chloride in aq. soln. is less ionized at  $0^\circ$  than at  $100^\circ$ . N. Tarugi and G. Bombardini's observations at the b.p., and F. G. Donnan and H. Bassett's observations at the f.p. The former conclude that complete non-ionized cobalt chloride can exist in red soln.

F. G. Donnan and H. Bassett extended the ionic hypothesis to include the formation of complex ions. The *complex-ion hypothesis* assumes that in addition to the simple  $Co^{++}$ -ions and  $Cl^-$ -ions, there are also complex anions, say  $CoCl_3^-$  and  $CoCl_4^{--}$ , in equilibrium such that the simple process of ionization  $CoCl_2 \rightleftharpoons Co^{++} + 2Cl^-$  is followed by  $CoCl_2 + 2Cl^- \rightleftharpoons CoCl_4^{--}$ , or by  $CoCl_2 + Cl^- \rightleftharpoons CoCl_3^-$ . The non-ionized salt in soln. is supposed to be blue, and the complex anion in soln. is also blue, whilst the colour due to the cobalt atom when outside the immediate sphere of the chlorine atoms, appears to be red. Thus, the colour produced by the free cobalt cations in aqueous soln. is red; whilst the red colour of the solid hexahydrate is doubtless due to the fact that the water molecules intervene between the cobalt and chlorine atoms. This is in accord with A. Werner's co-ordination theory. The colours exhibited by the double chlorides are attributed in the case of zinc chloride to the greater tendency of zinc to enter into negative complex groups, the zinc double chloride will have the constitution:  $Co-(ZnCl_4)$ , whilst the calcium double chloride will have the constitution:  $Ca-(CoCl_4)$ , since cobalt has a greater tendency to form negative complexes than calcium. In agreement with this, the former double salt is red, whilst the latter is blue. It is suggested that anhydrous, solid cobaltous chloride may not possess the simple formula  $CoCl_2$ , but may correspond to some polymeric complex form such as  $Co-(CoCl_4)$ , its colour being determined by the strong absorption in the red produced by the complex grouping,  $CoCl_4$ . It is, at all events, a curious fact that the pale blue, anhydrous chloride becomes reddish-violet at the temp. of boiling liquid air. As in the case of the soln. in alcohol and in conc. hydrochloric acid, this change of colour may be due to the breaking up of the complex grouping on lowering the temp. by an exothermic process. The work of H. G. Denham and co-workers, on transport numbers, of B. E. Moore, P. Job, J. Groh, and J. Groh and R. Schmidt, on absorption spectra, and of H. Bassett and H. H. Croucher, on the equilibria of the complex salt of cobalt chloride with hydrochloric acid, and mercuric, magnesium, and zinc chlorides, favours the complex ion hypothesis. A. Benrath's determination of the b.p. of aq. soln. indicates that

salts which form complexes with cobalt chloride favour the formation of red soln., and those which favour the blue colour do not form complexes.

P. Vaillant concluded from his observations on the absorption spectra of soln. of cobalt salts, that the cobalt ion possesses its own colour independently of the molecule, and the addition of a colourless electrolyte may modify the colour of a solution containing an electrolyte with a coloured ion, both by changing the ionization and by causing dehydration. These two actions are independent of each other, and the latter depends on the tendency of the added electrolyte to form hydrates. In organic solvents, the molecule is in a definite state of hydration, which is generally lower than that in which it exists in aq. soln. The organic solvent, like an added electrolyte, exerts a dehydrating action. It is assumed that the phenomena are best interpreted by the ionic hypothesis coupled with some form of the hydration theory, which, alone, does not adequately explain the observed facts. G. N. Lewis also concluded with F. G. Donnan and H. Bassett, that complex anions are formed in blue cobalt soln., but emphasized the need for the assumption that the change from blue to red is also attended by hydration. C. Mazzetti, and H. C. Jones and co-workers advocated the same hypothesis. This is a form of the *solvation theory*—1. 15, 11—where the cations are supposed to be loaded with water molecules. Water is produced or consumed in the formation of the complex ions:  $\text{CoCl}_2(\text{H}_2\text{O})_n + \text{Cl}'(\text{H}_2\text{O})_m \rightleftharpoons \text{CoCl}_3(\text{H}_2\text{O})_p + (n+m-p)\text{H}_2\text{O}$ . The solvation hypothesis was also discussed by H. C. Jones and H. P. Bassett, and E. O. Hulbert and co-workers. A. Kotschubey found that in these soln., the degree of solvation or hydration of the ions, and of the non-ionized salt, increases with dilution, and decreases with a rise of temp. A. Kotschubey did not accept the evidence that complex ions are formed in soln. of cobalt chloride, although he assumed that in red soln. containing mercuric, zinc, cadmium, stannous, or antimony chlorides, there are present complex ions of the type  $[\text{CoCl}_4(\text{ZnCl}_2)_2]''$ , and  $[\text{CoCl}_4(\text{HgCl}_2)_2]$ , but that the evidence for the formation of complexes of  $\text{CoCl}_4''$  by the action of hydrochloric acid, or of the chlorides of ammonium, potassium, magnesium, or aluminium, with cobalt chloride soln. is not definitely established. More recent work, however, has in general favoured the complex ion hypothesis. A. Kotschubey attributed the change in colour, not to the formation of  $\text{CoCl}_4'$ , but rather to the passage from the  $\text{Co}(\text{H}_2\text{O})_6^{++}$ -ion to the  $\text{Co}(\text{H}_2\text{O})_4^{++}$ -ion to  $[\text{Co}(\text{H}_2\text{O})_2\text{Cl}_2]$ .

R. Hill and O. R. Howell, and O. R. Howell suggested that the colour of cobalt compounds—red or blue—depends on the state of co-ordination of the cobalt atoms. If the atom is surrounded by six other groups or atoms, the colour is red; and if only four groups or atoms, the colour is blue—*e.g.*, in crystals of magnesium oxide, where each magnesium atom is surrounded by six oxygen atoms, if some of the magnesium are replaced by cobalt atoms, the colour is pink. This hypothesis does not agree with that of L. Pauling on the structure of the crystal lattice of the blue salt. In red, aq. soln., each cobalt atom is supposed, by R. Hill and O. R. Howell, to be surrounded by six water mols. H. Bassett and H. H. Croucher conclude that *red*, aq. soln. of cobalt chloride may contain one or more of the red cations,  $\text{Co}(\text{H}_2\text{O})_6^{++}$ ,  $\text{Co}(\text{H}_2\text{O})_4^{++}$ ,  $\text{Co}_2(\text{H}_2\text{O})_{10}^{++++}$ , or  $\text{Co}_2(\text{H}_2\text{O})_6^{++++}$ ; and *blue*, aq. soln. of cobalt chloride may contain the blue anions,  $\text{CoCl}_4''$ , or  $[\text{Co}(\text{H}_2\text{O})\text{Cl}_3]'$ . Other ions are also theoretically possible. The simple  $\text{Co}^{++}$ -ion is red, but is not likely to exist in aq. soln. When the chlorides of bivalent metals are dehydrated beyond the tetrahydrate, they generally become complex, and the complexity increases with increasing dehydration. Accordingly, dihydrated cobalt chloride is not simply  $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ , but rather  $(\text{CoCl}_2 \cdot 2\text{H}_2\text{O})_2$ , which may be either  $[\text{Co}(\text{H}_2\text{O})_4]^{++}[\text{CoCl}_4]''$  or else  $[\text{Co}(\text{H}_2\text{O})_3\text{Cl}]'[\text{CoCl}_3(\text{H}_2\text{O})]'$ .

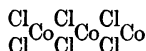
The colour of the ion does not appear to depend on its co-ordination, but only on its ionic state; nor do the number of charges carried by the ions appear to affect the colour appreciably. The manifestation of colour in compounds of metals like cobalt, is determined by the possibility of electron transference between different quantum levels. In the case of cobaltous compounds there are three electrons which may be considered to be

fairly mobile, but of these, two are on the outermost sheath and one on the next inner shell. If one or both of the two outer electrons have been lost (as in positive cobaltous ions with one or two positive charges), then the third electron can move freely between the inner and outer shells, but, the two outer positions being similar, it makes little difference to the colour whether one or both positions are empty. This state of affairs corresponds to that of the red, positive ions. The accumulation of electrons around the cobalt atom, as in  $[\text{Co}(\text{H}_2\text{O})_6\text{Cl}_3]$  and  $\text{CoCl}_4$ , tends to make one of the outer electrons move into an inner position, which is possible, since the third quantum group in the cobalt atom is not completely filled. The deep blue colour of the complex cobalt anions appears to arise in this way.

The behaviour of the non-ionic cobaltous compounds is rather more difficult to foresee. In a general way, since each valency electron of the metal is now replaced by a pair of shared electrons, the effect might be similar to that caused by the piling up of electrons in ions such as  $\text{CoCl}_4^{--}$ , and in many cobaltous compounds this actually seems to be the case. Anhydrous cobalt chloride, considered by us to be non-ionic, is pale blue, and we should expect the non-ionic  $[\text{Co}(\text{H}_2\text{O})_6\text{Cl}_3]$  also to be pale blue. The two shared electrons of a co-ordination covalency, when the co-ordination is to a neutral atom or molecule, clearly do not have this effect—doubtless because they are too firmly held by the atom to which they properly belong. In the cobaltous compounds they seem to exert little effect of any kind on the colour. In general, however, some effect would be expected, for the electronic environment, in which any electron-shifts occur in the outer levels of the ion, must depend to some extent on the number and nature of the atoms co-ordinated with the ion.

If the electron-shift which gives rise to the colour is that of an unshared electron—passing from the third to the fourth quantum level, or *vice versa*—then the compound in question has a red colour. If, however, the electron which moves between the two levels is one which is shared between the cobalt and another atom, *i.e.* a covalency electron, then a blue colour arises. It seems likely, however, that it is only indirectly of importance whether the moving electron is shared or unshared. The important point, in all probability, is that when an unshared electron is concerned, it is a  $3_z$  electron of the third quantum level which moves between the third and fourth quantum levels, whereas when a shared electron is concerned, it is a  $1_z$  electron of the fourth quantum level which makes the same jump.

The anhydrous salt when sublimed furnishes blue, loosely-coherent, crystalline spangles which feel like mica. W. Biltz reported the crystals to be hexagonal plates optically uniaxial, and with a negative birefringence. A. Ferrari said that the X-radiograms indicate that the pseudo-cubic lattice of the crystals is rhombohedral of the magnesium chloride type, having  $a=7.08$  Å., and  $c=17.35$  Å., and  $a:c=1:2.45$ , with 16 molecules per unit lattice. P. Niggli and W. Nowacki, R. J. Macwalter and S. Barratt, H. Grime and J. A. Santos, and V. M. Goldschmidt and co-workers discussed the subject. L. Pauling gave  $a=6.14$  Å., and added that each cobalt atom is probably surrounded by six chlorine atoms approximately at the corners of a regular octahedron, six edges of which are shared with other octahedra so as to form a layer. The cadmium chloride structure appears to be the stable one for substances of the type  $\text{MX}_2$ , where M has the co-ordination number 6, and the anion has a small polarizability. H. Bassett and H. H. Croucher assumed that the chlorine atoms are not ionized but are attached to the cobalt atoms by covalencies, the existence of the crystals being maintained by the six-co-ordinated condition of the metal atom. Each layer of octahedra in the crystals of cobalt can be regarded as a single, very complex molecule. The structure assumed by L. Pauling could result from the knitting together of a series of



chains containing four-co-ordinated cobalt. A. L. Potilitzin said that the monohydrate furnishes violet-blue, needle-like crystals; A. Ditte, that the hemihydrate furnishes dark bluish-violet, needle-like crystals; and J. Bersch, that the dihydrate furnishes a deep violet, crystalline powder, and the tetrahydrate peach-red crystals. H. Bassett and H. H. Croucher obtained the dihydrate as slender, purple prisms with oblique ends. A. Neuhaus said that the pseudo-rectangular crystals are monoclinic or triclinic. The twinning of the crystals of the dihydrate was studied by O. Lehmann. The hexahydrate furnishes red crystals, which, according to H. J. Brooke, belong to the monoclinic system having the axial

ratios  $a : b : c = 1.4788 : 1 : 0.9452$ , and  $\beta = 122^\circ 19'$ . O. Mügge gave  $a : b : c = 1.473 : 1 : 0.9445$ , and  $\beta = 57^\circ 46'$ . The (001)-cleavage is perfect, and the (110)-cleavage imperfect. The crystals were also examined by P. Groth, and J. C. G. de Marignac. O. Lehmann studied the twinning of the crystals; and O. Mügge, the pleochroism. The formation of large crystals in the magnetic field was observed by G. Roasio, and D. Samuracas.

The **specific gravity** of the anhydrous salt was found by L. Playfair and J. P. Joule to be 2.937; by A. Neuhaus, about 3.00; by G. P. Baxter and F. B. Coffin, 3.348 at  $25^\circ/4^\circ$ ; by G. L. Clark and co-workers, 3.356 at  $25^\circ/4^\circ$ ; and W. Biltz and E. Birk, 3.367 at  $25^\circ/4^\circ$ . A. Ferrari calculated 3.43 from the X-radiogram data. C. H. D. Bödeker gave 1.84 at  $13^\circ$  for the sp. gr. of the hexahydrate; A. Neuhaus gave 2.42; B. Gossner, 1.917; P. A. Favre and C. A. Valson, 1.898 at  $23.9^\circ$ ; and G. L. Clark and co-workers, 1.924 at  $25^\circ/4^\circ$ . A. Neuhaus also gave 2.216 for the sp. gr. of the tetrahydrate, and 2.42 for the dihydrate. G. L. Clark and co-workers gave 2.479 at  $25^\circ/4^\circ$  for the sp. gr. of the dihydrate. The sp. gr. of soln. of cobalt chloride were measured by B. Franz, G. T. Gerlach, R. Wagner, P. A. Favre and C. A. Valson, G. Quincke, W. Biltz, R. Engel, P. F. Gaehr, O. R. Howell, J. Trötsch, W. W. J. Nicol, A. E. Oxley, J. Wagner, J. Grailich, P. Sabatier, H. C. Jones and co-workers, A. Heydweiller, L. Brant, G. Dreyer, S. Lussana and G. Bozzola, P. Moretto, and R. Wernicke. The results indicate the sp. gr. of soln. with :

CoCl <sub>2</sub>	.	.	1	2	4	6	8	10 per cent.		
Sp. gr.	{	18°/4°	.	.	1.0076	1.0168	1.0356	1.0549	1.0747	1.0949
		20°/4°	.	.	1.0073	1.0165	1.0350	1.0538	1.0735	1.0940
		25°/4°	.	.	1.0069	1.0150	1.0335	1.0525	—	—

B. Franz's values are :

CoCl <sub>2</sub>	.	.	.	1	5	10	12	20	25 per cent.
Sp. gr. at $17.5^\circ$	.	.	.	1.0099	1.0496	1.0997	1.1579	1.2245	1.3002

R. Wagner gave for the sp. gr. of  $N$ -,  $\frac{1}{2}N$ -,  $\frac{1}{4}N$ -, and  $\frac{1}{8}N$ -CoCl<sub>2</sub>, the respective values 1.0571, 1.0286, 1.0144, and 1.0058. P. A. Favre and C. A. Valson, and G. G. and I. N. Longinescu discussed the calculated and observed sp. gr. of soln. B. Cabrera and co-workers gave for the sp. gr. of soln. with 0.1065 gm. of CoCl<sub>2</sub> per gram of soln. at  $\theta$ ,  $1.1018\{1 - 0.00025(\theta - 20)\}$ ; and for soln. with 0.3206 gm. of CoCl<sub>2</sub> per gram of soln.,  $1.3630\{1 - 0.0003(\theta - 20)\}$ . C. Winkler said that the sat. soln. in alcohol of sp. gr. 0.792 has a sp. gr. of 1.0107, and contains 23.66 per cent. CoCl<sub>2</sub>. P. Moretto, and S. Lussana and G. Bozzola discussed the temp. of **maximum density**; and G. Dreyer gave for soln. with 0.883, 1.828, and 1.859 per cent. CoCl<sub>2</sub>, the lowering of the temp. of maximum density of water (3.96), respectively  $1.09^\circ$ ,  $2.36^\circ$ , and P. A. Favre and C. A. Valson found that with  $N$  gram-equivalent of cobalt chloride per kgrm. of water, the sp. gr. of soln. at  $23.9^\circ$ ; the vol. obtained by dividing the total weight of water and salt by the sp. gr.; and the successive increments in vol. produced by adding another eq. of salt, were as follows :—

$N$ gram-equivalents	.	1	2	3	4	5	6	9.
Sp. gr.	.	1.055	1.101	1.141	1.177	1.209	1.238	1.309
Total volume	.	1061	1124	1189	1254	1319	1384	1582
Increments in volume	.	61	63	65	65	65	65	66

R. Engel, O. R. Howell, and J. Kendall and K. P. Monroe measured the sp. gr. of soln. in hydrochloric acid; C. Winkler, in ethyl alcohol; and A. Naumann and E. Vogt, in acetone. G. L. Clark and co-workers gave 38.70 for the **molecular volume** of the anhydrous salt at  $25^\circ$ ; and W. Biltz and E. Birk, 38.58 at  $25^\circ$ . W. Biltz, E. Moles, I. I. Saslawsky, and U. Panichi studied the observed and calculated mol. vol. H. H. Stephenson calculated a 32 per cent. contraction, and G. L. Clark and H. K. Buckner, a 25.86 per cent. contraction. G. L. Clark and co-workers gave 123.69 for the mol. vol. of the hexahydrate; and G. L. Clark and

H. K. Buckner, 15.9 per cent. for the contraction in the reaction:  $\text{CoCl}_2 + 6\text{H}_2\text{O} = \text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ . A. Balandin made observations on the subject; and E. N. Gapon studied the relation between the m.p. and sp. gr. of the hexahydrate. G. L. Clark and co-workers observed a 20.91 per cent. contraction in the reaction:  $\text{CoCl}_2 + 2\text{H}_2\text{O} = \text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ . F. Ephraim, R. Reinicke, and W. Fischer studied the mol. vol. of the salt; and W. W. J. Nicol discussed the mol. vol. of the soln. P. Vinassa discussed the mol. number; and G. Tammann, the **inner pressure** of soln. The coeff. of **diffusion** of soln. in agar-agar with 4.72 mgrms. per c.c., were found by F. Voigtländer to be 0.443, 0.83, and 1.33 sq. cm. per day respectively, at 0°, 26°, and 40°. Observations were also made by E. Rona, J. H. Long, M. Torre, and J. Schuhmeister; the last-named gave for a soln. with 1.5 gram-equivalents per litre at 18°, 0.46 grm. per sq. cm. per day. E. Rona measured the rate of diffusion in hydrochloric acid soln. O. R. Howell found the **surface tension** of a soln. of 120 grms. of the hexahydrate per litre at 20° to be 74.36 dynes per cm. Z. H. Skraup and co-workers studied the capillary rise in filter-paper; M. Padoa and G. Tabellini, the drop weight of molar soln. at different temp.; and H. Auer, the effect of a magnetic field of 20,000 gauss on the surface tension. O. R. Howell measured the surface tension of soln. in hydrochloric acid; and P. P. and N. S. Kosakewitsch, in alcoholic soln. R. Wagner gave for the **viscosity** of  $N$ -,  $\frac{1}{2}N$ -,  $\frac{1}{4}N$ -, and  $\frac{1}{8}N$ -soln. at 25°, respectively 1.2041, 1.0975, 1.0482, and 1.0078—water unity. Measurements were made by O. R. Howell, and M. R. Schmidt and H. C. Jones. C. Mazzetti gave for the coeff. of viscosity,  $\eta$ , of soln. with  $C$  gram-equivalent of cobalt chloride per litre:

$C$		0.251	0.752	1.504	2.006	7.631
$\mu$	$\left\{ \begin{array}{l} 13^\circ \text{ to } 14^\circ \\ 34^\circ \text{ to } 35^\circ \\ 45^\circ \text{ to } 46^\circ \\ 59^\circ \text{ to } 60^\circ \end{array} \right.$	$\left\{ \begin{array}{l} . \\ . \\ . \\ . \end{array} \right.$	$\left\{ \begin{array}{l} . \\ . \\ . \\ . \end{array} \right.$	$\left\{ \begin{array}{l} . \\ . \\ . \\ . \end{array} \right.$	$\left\{ \begin{array}{l} . \\ . \\ . \\ . \end{array} \right.$	$\left\{ \begin{array}{l} . \\ . \\ . \\ . \end{array} \right.$
		0.01278	0.01346	0.01515	0.01648	0.05983
		0.00821	0.00881	0.00975	0.01044	0.03303
		0.00662	0.00725	0.00796	0.00850	0.02548
		0.00516	0.00570	0.00636	0.00675	0.01911

O. R. Howell, J. Kendall and K. P. Monroe, G. Matsuo and co-workers, and N. A. Yajnik and R. L. Uberoy measured the viscosity of soln. in hydrochloric acid; M. R. Schmidt and H. C. Jones, of soln. in methyl alcohol, in ethyl alcohol, and in glycerol. G. Nagel discussed the surface phenomena of soln. of the salt.

H. Feudt found that the **specific heat** of soln. containing 16.4 per cent. of  $\text{CoCl}_2$  is 0.767 between 15° and 49°, and 0.787 between 18° and 89°; and soln. with 8.9 per cent. of  $\text{CoCl}_2$ , the sp. ht. is 0.865 between 15° and 49°, and 0.896 between 19° and 90°. The subject was studied by K. Jauch. W. Wrewsky measured the sp. ht. of soln. in ethyl alcohol. L. R. von Fellenberg, and C. Sandonnini said that cobalt chloride sublimates without fusing, and J. L. Proust, after fusing. A. Ferrari and co-workers gave 724° for the **melting-point** of anhydrous cobalt chloride, in a current of hydrogen chloride; H. Bassett and W. L. Bedwell gave 735°; and A. Ferrari, and A. Ferrari and A. Baroni noted that the presence of nickel chloride raises the m.p. W. Hempel and H. Thiele were unable to volatilize cobaltous chloride at ordinary press. or in vacuo; but W. Biltz and E. Birk found that the chloride first melts and then boils to furnish a pale blue sublimate, and the sublimation of cobalt chloride was discussed by A. Gorgeu, W. Spring, R. Rieth, and C. Winkler. According to L. R. von Fellenberg, cobalt chloride is volatile at a red-heat in a current of hydrogen chloride; and G. L. Clark and co-workers found that sublimation occurs below 500° in the presence of a little hydrogen chloride. C. G. Maier obtained 1049° for the **boiling-point** of the anhydrous chloride; and for the **heat of vaporization**, in Cals. per mol., by extrapolation of the vap. press.:

	1049°	1017°	972.4°	900.2°	805.2°	730.0°
Heat of vaporization .	30.61	29.70	28.52	25.75	22.41	20.19

K. Jellinek and R. Uloth calculated the dissociation pressure of cobalt chloride,  $\text{CoCl}_2 \rightleftharpoons \text{Co} + \text{Cl}_2$ , and obtained for the partial press. of the chlorine,  $p$  mm.:

	25°	400°	500°	600°
$p$ . . . . .	$4.57 \times 10^{-55}$	$9.55 \times 10^{-18}$	$2.34 \times 10^{-14}$	$6.61 \times 10^{-12}$

J. Bersch said that at 30° the red hexahydrate begins to turn blue in places, at 35° the whole mass appears dark blue, and at 35° to 39° it loses its lustre, and breaks up to form a mass of acicular crystals; if the product be melted and cooled, the original red mass of crystals is formed. J. Bersch gave 86·75° for the m.p. of the hexahydrate; this temp. appears to be too high, because W. Stortenbeker, and A. L. Potilitzin found that dry crystals melt at about 54°, a little higher than the transition temp. of the hexahydrate to the dihydrate. J. Bersch said that the melt may be undercooled to 50° without solidification. A. Hantzsch observed an incongruent m.p. at 35°. G. N. Wyrouboff studied the **dehydration** of the salt; he observed that the salt partially melts at 60° and then appears blue. If kept many hours at this temp., it gradually loses water, and becomes deeper blue. Under the microscope the salt then appears as a mixture of red crystals which have not melted, and opaque crystals of a lower hydrate, swimming in a soln. intensely blue. If the temp. rises to 80°, more water is given off, and when the weight is constant at this temp., the deep violet salt appears homogeneous, and it corresponds approximately with the monohydrate, and loses water only when the temp. rises to 135° to 140°. According to A. L. Potilitzin, the hexahydrate loses no perceptible quantity of water in an open tube, but it becomes turbid at 30° to 40°, and at 45° to 52° it rapidly effloresces, and after being kept 4 hrs. at this temp. its composition approximates to the rose-red dihydrate. In dry air, over sulphuric acid, at ordinary temp., the salt also passes slowly into the dihydrate. J. Bersch found that the red hexahydrate approximates to the tetrahydrate at 11°, and to the dihydrate at 121°. According to A. Hantzsch and F. Schlegel, J. Bersch, P. Sabatier, and E. J. Mills, the hexahydrate loses 4 mols. of water in a desiccator over sulphuric acid. H. Lescœur, and W. Müller-Erbach made observations on the vap. press. of the hydrates, and observed that no hydrate between the di- and hexa-hydrate exists at 20°. H. Lescœur gave 4·0 mm. for the vap. press. of the hexahydrate at 20°, and 14·9 mm. at 40°. According to H. Wessels, if a tube of compressed, powdered hexahydrate be warmed to 63° at one end, clear layers of the anhydrous salt, the dihydrate, and the hexahydrate, and water travel to the cold part of the tube.

C. G. Maier measured the **vapour pressure** of the anhydrous chloride,  $p$  mm., at different temp., and found at :

	633·3°	699·2°	799·1°	915·7°	957·7°	991·4°	1010·4°	1024·5°	1035·1°	1091·2°
$p$	121·4	145·9	211·4	364·9	484·4	604·1	685·4	764·8	829·6	1256·7

G. Tammann gave for the lowering of the vap. press. of aq. soln. by the dissolution of 6·05, 24·04, 41·47, and 57·69 grms. of salt per 100 grms. of water, respectively, 13·9, 75·2, 146·3, and 207·5 mm. G. Charpy obtained for the vap. press.,  $p$  mm., of a 32 per cent. soln. of cobaltous chloride :

	21°	35°	40°	59°	70°	80°	88°
$p$	7	15	19	39	59	93	120 mm.

G. Charpy added that the corresponding curve includes to almost linear parts one ranging from 20° to 40° corresponding with the red soln., and the other, ranging above 75°, with the blue soln. The intermediate part is curved. The curves thus indicate the existence of two stable modifications of the salt—hydrates or other molecular aggregates. The curve is similar to the solubility curve of A. Étard, but the critical points do not coincide. Measurements were also made by R. E. Wilson, K. Jellinek and R. Uloth, R. Uloth, W. Geller, and N. Tarugi and G. Bombardini. M. Prud'homme studied the relation between the mol. wt. and the lowering of the vap. press. of aq. soln. I. H. Derby and V. Yngve, and C. Dieterici measured the vap. press. of the hydrated chloride, and of its sat. soln., and the results show that for sat. soln. of concentration,  $C$ , the vap. press.,  $p$  mm., at  $\theta$ , are :

	24·19°	28·68°	39·47°	49·23°	52·25°	56·44°	68·26°	78·87°
$p$	14·7	18·4	30·5	44·8	48·6	58·7	105·1	170·9
	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$				$\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$			

The results are plotted in Fig. 77. The transition temp. for  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O} \rightleftharpoons \text{CoCl}_2 \cdot 2\text{H}_2\text{O} + 4\text{H}_2\text{O}$  is  $52.25^\circ$ . No evidence of the existence of a tetrahydrate was observed; nor did the observations of H. Lescœur, on the vap. press. during the dehydration of the hexahydrate, show any evidence of the existence of the tetrahydrate.

F. Rüdorff gave for the **cryohydrates**—the ice-line on the solubility curve, Fig. 78—for soln. with 15.3 and 22.5 per cent. of  $\text{CoCl}_2$ , respectively,  $-10.0^\circ$ , and  $-20.0^\circ$ . This does not fit F. Guthrie's value  $-15.3^\circ$  for the **eutectic**, since the extrapolated value from the data of F. Rüdorff, and A. Étard, is  $-22.5^\circ$  for soln. with 24 per cent.  $\text{CoCl}_2$ . The **molecular weight** determinations of cobalt chloride in boiling pyridine, and piperidine, by A. Werner; in boiling quinoline, by E. Beckmann; and in boiling bismuth chloride, by L. Rügheimer, agree with the simple formula,  $\text{CoCl}_2$ ; but in freezing urethane, N. Castoro found that the results agreed with the doubled formula,  $\text{Co}_2\text{Cl}_4$ ; but G. Bruni and A. Manuelli could not confirm this. The **lowering of the freezing-point** of aq. soln. was measured by R. E. Hall and W. D. Harkins, W. Biltz, A. Benrath, N. Tarugi and G. Bombardini, and H. C. Jones and co-workers. The results showed that a soln. with  $G$  grm. of  $\text{CoCl}_2$  per 100 grms. of water had a f.p. of :

$G$	0.0225	0.1159	0.831	3.601	5.4775	11.691	25.98
F.p.	$-0.00930^\circ$	$-0.04575^\circ$	$-0.325^\circ$	$-1.3934^\circ$	$-2.1900^\circ$	$-5.420^\circ$	$-19.000^\circ$

The **raising of the boiling-point** of aq. soln., measured by R. Salvadori, N. Tarugi and G. Bombardini, and A. Benrath, showed that soln. with 0.80, 2.23, and 7.88 grms. of  $\text{CoCl}_2$  in 100 grms. of water, raised the b.p. respectively,  $0.11$ ,  $0.30^\circ$ , and  $1.0^\circ$ . R. Salvadori, and O. E. Frivold measured the raising of the b.p. in methyl alcohol; A. Benrath, and O. E. Frivold, in ethyl alcohol; A. L. Robinson, in acetone; A. Werner, in pyridine; E. Beckmann, in quinoline; and L. Rügheimer, in bismuth chloride.

The **heat of formation** of anhydrous cobaltous chloride is, according to J. Thomsen,  $(\text{Co}, \text{Cl}_2) = 76.48$  Cals; and, according to W. Biltz and W. Holverscheid,  $74.8$  Cals. The subject was studied by E. Rabinowitsch and E. Thilo, O. Schütz and F. Ephraim, F. Ephraim, and G. Devoto and A. Guzzi. J. Thomsen gave  $(\text{Co}, \text{Cl}_2, \text{Aq.}) = 94.824$  Cals.;  $(\text{Co}, 2\text{HCl}, \text{Aq.}) = 16.184$  Cals.; and for the **heat of neutralization**,  $\{\text{Co}(\text{OH})_2, 2\text{HCl}, \text{Aq.}\} = 21.14$  Cals.; M. Berthelot gave  $(\text{CoO}, 2\text{HCl}, \text{Aq.}) = 21.1$  Cals.; W. Biltz and W. Holverscheid,  $(\text{Co}, 2\text{HCl}, 8.8\text{H}_2\text{O}) = 13.4$  Cals.; and F. Bourion,  $4\text{CoO} + 4\text{S}_2\text{Cl}_2 = 4\text{CoCl}_2 + 2\text{SO}_2 + 6\text{S} + 124$  Cals. J. Bersch noted that cooling occurs when the hexahydrate is dissolved in water; and F. G. Donnan and H. Bassett, that heat is developed when a conc. aq. soln. is diluted. J. Thomsen gave for the **heat of solution** of the hexahydrate in 400 mols. of water at  $18^\circ$ ,  $-2.85$  Cals.; and P. Sabatier gave for the dihydrate,  $9.85$  Cals; and J. Thomsen, for the anhydrous chloride,  $18.3$  Cals. at  $21.5^\circ$ ; and J. Thomsen gave for the heat of hydration  $(\text{CoCl}_2, 6\text{H}_2\text{O}) = 21.19$  Cals.; P. Sabatier,  $(\text{CoCl}_2, 2\text{H}_2\text{O}, 4\text{H}_2\text{O}) = 6.95$  Cals.; and  $(\text{CoCl}_2, 2\text{H}_2\text{O}) = 5.7$  Cals. G. Devoto and A. Guzzi calculated  $41,900$  cal. for the **free energy** of formation of the molten salt; and G. Beck,  $255,000$  cal. for the total energy of the reacting electrons. W. Klemm studied the relation between the lattice energy and the heat of formation.

A. Neuhaus gave for the **indices of refraction** of the dihydrate,  $\alpha = 1.625$ ,  $\beta = 1.671$ , and  $\gamma = 1.670$ . H. C. Jones and F. H. Getman found the refractive indices of soln. with  $M$  mol. of the salt per litre :

$M$	0.0969	0.1279	0.1918	0.3197	0.4475	0.5114	0.6393
$\mu$	1.32735	1.33005	1.33151	1.33518	1.33910	1.34064	1.34415

A. Bromer gave for soln. with  $P$  per cent. of cobaltous chloride, with the  $C$ -,  $D$ -,

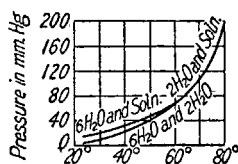


FIG. 77.—Vapour Pressures of Hydrates and Saturated Solutions of Cobaltic Chloride.



and *F*-lines, at 20°, and the mol. refraction, *R*, with the  $\mu^2$ -formula, and the *D*-line :

<i>P</i>		$\mu_C$	$\mu_D$	$\mu_F$	<i>R</i>
5.784	.	1.34473	1.34738	1.34801	17.94
0.082	.	1.33120	1.33345	1.33431	16.20

Observations were also made by J. Grailich, A. Heydweiller, L. R. Ingersoll, P. Vaillant, O. R. Howell, and G. Limann. A. Heydweiller made observations on the dispersion. J. H. Gladstone and W. Hibbert found the **molecular refraction**, with the  $\mu$  formula, for soln. having 4.97, 9.47, 17.49, and 27.86 per cent. of cobalt chloride, to be respectively, 32.86, 32.77, 32.84, and 32.71 for the *H<sub>a</sub>*-line, and 33.53, 32.99, 33.12, and 32.97 for the *D*-line. F. W. O. de Coninck found that the red, aq. soln. becomes violet on exposure to sunlight; and that only six-tenths of the light transmitted by the red soln. is transmitted by the blue soln. Attempts to isolate the blue product were not successful.

R. A. Houstoun, and H. M. Vernon discussed the changes of colour which occur when aq. soln. of the salt are diluted, and the temp. is raised—*vide supra*, the colour of cobalt chloride. The anhydrous chloride is blue, like all co-ordinated, unsaturated cobalt salts; whereas co-ordinated, saturated salts are red. E. N. da C. Andrade observed that cobalt chloride in a flame containing chlorine, gives a **molecular spectrum** with bands in the green and blue. H. Fesefeldt studied the absorption spectrum of the thin layers of anhydrous chloride and observed characteristic bands between 200 and 240m $\mu$ . The absorption spectrum of aq. soln.—*vide supra*, the absorption spectrum of cobalt chloride—was observed by W. V. Bhagwat and N. R. Dhar, R. Brdicka, W. R. Brode, W. R. Brode and R. A. Morton, A. R. Brown, W. W. Coblenz and co-workers, F. L. Cooper, A. Cotton, G. Déniges, G. J. Elias, A. Étard, J. Formanek, J. Groh, A. Hantzsch, W. Hardt, W. N. Hartley, R. Hill and O. R. Howell, S. M. Karim and R. Samuel, R. A. Houstoun and co-workers, E. O. Hulbert and co-workers, T. Inoue, H. C. Jones and co-workers, J. von Koczkas, R. J. Macwalter and S. Barratt, C. Mazzetti, M. G. Mellon, B. E. Moore, A. Rosenheim and V. J. Meyer, W. J. Russell, S. B. Schwezoff and A. M. Tanchilewitsch, Y. Shibata and T. Inoue, G. Spacu and J. G. Murgulescu, O. Specchia, P. Vaillant, and H. W. Vogel. O. Stelling, and S. Aoyama and co-workers studied the **X-ray absorption spectrum**. O. Gossmann observed no **emission of ions** by cobaltous chloride at 450°. R. Robl observed no **luminescence** in ultra-violet light; and M. Trautz detected neither **crystallo-luminescence** nor **triboluminescence**, with the anhydrous salt nor with the hexahydrate.

R. W. Roberts and co-workers, F. Allison and E. J. Murphy, and E. Miescher found that the **magnetic rotation** of cobalt chloride is positive. R. Wasmuth gave 0.8224 for the sp. rotation, and 5.9215 for the mol. rotation of cobalt chloride in soln. containing 14.603 grms. of chloride per 100 c.c. with Na-light. G. J. Elias studied the results with hydrochloric acid soln. L. R. Ingersoll gave for **Verdet's constant**, with layers 1 cm. thick per gauss, with a soln. of sp. gr. 1.296 at 23°, 0.0096 and 0.0066 for light of wave-length, respectively, 0.8 and 1.0 $\mu$ . Observations were also made by E. Miescher, O. Schönrock, and M. Scherer. P. Krishnamurti studied the **Raman effect**.

W. Hampe found that the **electrical conductivity** of molten cobaltous chloride is very good—chlorine is evolved at the anode, and crystalline cobalt is deposited at the cathode. E. Franke gave for the mol. electrical conductivity,  $\mu$ , of a soln. of a mol. of cobaltous chloride in *v* litres of water at 25° :

<i>v</i>	.	.	32	64	128	256	512	1024
$\mu$	.	.	100.5	105.3	110.3	114.0	116.8	118.7

Observations were also made by W. Althammer, W. Hardt, A. Heydweiller, H. C. Jones and co-workers, C. Mazzetti, A. Rosenheim and V. J. Meyer, M. R. Schmidt and H. C. Jones, N. Tarugi and G. Bombardini, O. R. Howell, and J. Trötsch. The

limiting value of the conductivity at 18°, found by A. Heydweiller, is  $\lambda_{\infty}=108$ ; W. Althammer gave 125.6 to 126.9 at 25°; and C. Mazzetti, 102 at 10°; 143 at 20°; 184 at 30°; 224 at 40°; 260 at 50°; and 289 at 60°. According to C. Mazzetti, if  $C$  denotes the number of gram-equivalents of cobalt chloride per litre, the eq. conductivity,  $\lambda$ , are :

$C$	.	.	.	.	0.251	0.752	1.504	2.006	7.631
$\lambda$	13° to 14°	.	.	.	0.0705	0.0605	0.0511	0.0460	0.0112
	34° to 35°	.	.	.	0.1058	0.0886	0.0742	0.0665	0.0174
	45° to 46°	.	.	.	0.1252	0.1040	0.0869	0.0777	0.0208
	59° to 60°	.	.	.	0.1465	0.1209	0.1012	0.0904	0.0249

Curves showing the relation between eq. conductivity show a point of inflexion which indicates that two distinct curves are involved, and that the phenomenon is due to a reduction in the degree of hydration of the ions as the concentration increases, so that the eq. conductivity falls less rapidly than would otherwise be anticipated. The results with mixed soln. of barium and cobalt chlorides are attributed to a decrease in the hydration of the ions as the concentration increases, and to the formation of complex anions. H. C. Jones and co-workers, J. Trötsch, E. Rimbach and K. Weitzel, and F. G. Donnan and H. Bassett studied the temp. coeff. of the conductivity.

The effect of temperature on the conductivity of the soln. of cobalt chloride was also studied by G. Dickhaus, and J. Hamacher; the results show breaks in the regularity of the curve between 31.4° and 31.5°, between 40.9° and 41.0°, and 47.6° and 47.7°. W. Geller, and G. Charpy also observed breaks in the curves for the vapour press. of the soln. H. F. Haworth studied the conductivity with alternating currents. O. R. Howell measured the electrical conductivity of soln. in hydrochloric acid; P. B. Davis and co-workers, soln. in formamide; W. Hardt, E. Rimbach and K. Weitzel, H. R. Kreider and H. C. Jones, and H. C. Jones and L. McMaster, soln. in methyl alcohol; and E. Rimbach and K. Weitzel, H. C. Jones and L. McMaster, A. Rosenheim and V. J. Meyer, B. Völlmer, M. R. Schmidt and H. C. Jones, and H. R. Kreider and H. C. Jones, soln. in ethyl alcohol. W. Hardt measured the equivalent conductivity,  $\lambda$ , of an eq. of cobalt chloride in  $v$  litres of alcohol at 20°, and obtained the results summarized in Table IV. He also

TABLE IV.—EQUIVALENT CONDUCTIVITIES OF MIXED SOLUTIONS OF COBALTOUS CHLORIDE IN ETHYL ALCOHOL AND WATER.

$v$	Percentage proportion of ethyl alcohol						
	100	85	70	50	40	30	0
1	2.0	6.5	10.7	17.6	21.0	24.8	63.2
2	2.3	8.8	13.7	20.5	24.5	30.7	72.5
4	2.7	11.1	16.7	23.2	27.9	35.6	80
8	3.15	13.1	19.2	25.6	30.9	39.7	87.2
16	3.8	15.1	21.7	27.9	33.4	43.2	92.8
32	4.7	17.1	24.0	30.5	35.7	45.3	96.8
64	6.0	19.2	26.1	31.7	37.2	47.2	102.0
128	7.5	21.0	27.8	33.1	38.4	48.9	105.6
256	9.2	22.6	29.1	34.3	39.6	50.3	107.6
512	10.7	23.8	30.2	35.3	40.4	51.2	109.8
1024	13.3	25.2	31.2	36.1	41.2	51.9	110.6
2048	16.6	26.1	31.8	36.7	41.8	52.5	110.8
4096	20.0	27	32.4	37.1	42.2	52.7	111.0

obtained results for methyl and amyl alcohols. The eq. conductivity of soln. in methyl alcohol is 32.2; in ethyl alcohol, 4.9; and in amyl alcohol, 0.057 under analogous conditions. F. Baur, E. Rimbach and K. Weitzel, H. C. Jones and L. McMaster, and M. Wien measured the electrical conductivity of soln. in acetone;

A. Hantzsch, S. von Laszczynsky and S. von Gorsky, A. T. Lincoln, and J. N. Pearce, of soln. in pyridine; and J. N. Pearce, of soln. in quinoline.

The **transport numbers** of the anion were found by W. Althammer for dilutions of a mol. of the salt, in  $v$  litres, at  $18^\circ$ , to be 0.6067 for  $v=49.73$ , 0.6010 for  $v=98.19$ , and 0.6016 for  $v=193.4$ . Observations were also made by W. Bein, E. Rona, and A. Kotschubey. C. Mazzetti found that the ratio of the mobility of the cobalt ion to the fluidity of water at the same temp. increases as the temp. rises from  $10^\circ$  to about  $30^\circ$ , and then diminishes regularly with rise of temp. This divergence is attributed to an independent increase in the value of the eq. conductivity, owing to the de-solvation of the cobalt ion. The increase in the transport number of the anion with increased concentration of the soln., is attributed in part to the formation of complex anions. H. G. Denham found the transport numbers,  $n$ , of cobalt,  $\text{Co}^{++}$ , in soln. of the chloride with  $C$  mols.  $\text{CoBr}_2$  per litre, to be:

$C$	.	.	.	0.090	0.459	1.345	2.448	3.106	4.731	5.554
$n$	.	.	.	0.409	0.413	0.340	0.322	0.215	0.005	-0.444

The decreasing values and the negative value correspond with the formation of complexes  $\text{CoBr}_3'$  and  $\text{CoBr}_4''$  as increasing amounts of cobalt are transferred to the anode.

H. C. Jones and co-workers, and P. Vaillant calculated the degree of **ionization** of the salt in aq. soln. from electrical conductivity measurements. A. Günther-Schulze inferred that in conc. soln., the ionization proceeds:  $\text{CoCl}_2 \rightleftharpoons \text{CoCl}' + \text{Cl}'$ ; and in soln. with less than normal concentration,  $\text{CoCl}_2 \rightleftharpoons \text{Co}^{++} + 2\text{Cl}'$ . For the factor  $i$  calculated from the lowering of the b.p., for soln. with  $C$  eq. of the salt per litre, R. E. Hall and W. D. Harkins observed:

$C$	.	.	.	0.005	0.01	0.02	0.05	1.00
$i$	.	.	.	2.858	2.802	2.749	2.687	2.650

Observations were also made by R. Salvadori; N. Tarugi and G. Bombardini calculated values from the lowering of the vap. press., and the ionization of the salt in aq. soln. was discussed by W. H. Banks and co-workers. G. N. Lewis and G. A. Linhart calculated the activity coeff. from observations on the f.p. of aq. soln. of  $C$  mol. of the salt in a litre of water and found for  $C=10^{-2}$ ; 0.00943 for  $C=10^{-4}$ ; and 0.00995 for  $C=10^{-7}$ . H. Ley inferred that the **hydrolysis** of aq. soln. is very small; and L. Bruner observed no hydrolysis at  $40^\circ$  by the method of sugar inversion. R. Engel observed some hydrolysis, and W. Althammer said that at  $25^\circ$  the hydrolysis:  $\text{CoCl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{CoCl}(\text{OH}) + \text{HCl}$  occurs to the extent of 0.12 per cent. for soln. with 0.05 mol. per litre, and 0.53 per cent. for soln. with 0.01 mol. per litre. C. Kullgren gave for soln. with  $v=16$  and 64, a percentage hydrolysis of 0.0173 and 0.0147, respectively at  $85.5^\circ$ , and at  $100^\circ$ , of 0.0172 and 0.0196, respectively. H. G. Denham obtained a hydrolysis of 0.11 per cent. at  $25^\circ$  for  $v=16$ , and 0.17 per cent. for  $v=32$ . Observations were made by T. Katsurai, H. M. Vernon, and R. Brdicka. H. G. Denham measured the e.m.f. of the cell  $(\text{Pt})\text{H}_2|\text{CoCl}_2 \text{ soln.}, \text{NH}_4\text{NO}_3 \text{ sat. soln.}|\text{N-KCl}, \text{Hg}_2\text{Cl}_2\text{-electrode}$  for a soln. of a mol of cobalt chloride in 0.5 litre of water, and calculated for the corresponding **H<sup>+</sup>-ion concentration**:

	26°	48°	67°	84.5°	91°	100°
Electromotive force . . .	0.4996	0.4917	0.4834	0.4659	0.4566	0.4382
H <sup>+</sup> -ion concentration $\times 10^3$ .	0.213	0.523	1.064	2.612	3.945	7.943

The **solvation** of the salt in soln. was discussed in connection with the colour. H. C. Jones and co-workers calculated the degree of solvation, i.e. the degree of hydration of the salt, expressed as the number of mols. of water in combination with a mol. of the salt at the given concentration of  $M$  mols per litre when a litre of the soln., at that concentration contained 1000 grms. of water; and found:

$M$	.	.	.	0.025	0.075	0.100	0.500	1.00	1.50	2.00
Hydration . . .	.	.	.	152.88	33.68	34.13	27.86	24.14	21.1	17.88

H. J. Blikslager studied the formation of complex ions in the electrolysis of soln. of the cobalt chloride in fused alkali chlorides; and R. Böttger, and G. Gore, the **electrodeposition** of cobalt from soln. of cobalt salts—*vide supra*. G. Devoto and A. Guzzi found that the **decomposition potentials**,  $E$  volt, of the molten salt, at different temp., are:

	750°	800°	850°	900°
$E$ . . . . .	0.948	0.914	0.882	0.860

M. le Blanc found the decomposition tension of  $N\text{-CoCl}_2$  is 1.78 volt. R. Brdicka found the decomposition potential of cobalt from blue soln.—*vide supra*, deposition potential of cobalt—is greater than with pink soln., indicating a greater activity of the  $\text{Co}^{++}$  ions in blue soln. W. Althammer found the **electromotive force** of the cell  $(\text{Pt})\text{H}_2|\text{CoCl}_2 \text{ soln.}|\text{KCl}_{\text{sat. soln.}}|0.1N\text{-KCl}, \text{Hg}_2\text{Cl}_2|\text{Hg}$  to be constant after about half an hour, and to be 0.579 volt with 0.05M-CoCl<sub>2</sub>, and 0.583 volt with 0.01M-CoCl<sub>2</sub>. T. Svensson studied the cell  $\text{Pt}|0.1M\text{-CoCl}_2|N\text{-KCl},|\text{Hg}$ ; and H. G. Denham, the cell indicated above. G. Tammann and H. O. von Samson-Himmelsjerna studied the potential of cobalt soln. of the chloride. The electrolysis of conc. aq. soln. of cobaltous chloride with platinum electrodes was found by J. H. Paterson to furnish cobalt metal, and with dil. soln., and low current densities, cobalt hydroxide; and M. le Blanc found that with  $N\text{-CoCl}_2$ , and a current of 1.78 volts; the platinum anode acquires a film of cobalt peroxide. C. Schall studied the anodic oxidation of soln. of cobaltous salts—*vide supra*, the electrodeposition of cobalt; and G. N. Lewis and G. A. Linhart, and K. Hess and K. Jellinek, the activity coeff. H. N. Holmes studied the **electrostenolysis** of soln. of cobalt chloride; and A. L. T. Moesveld and H. J. Hardon, the **electrostriction** of aq. soln. of cobalt salts.

G. Wiedemann measured the **magnetic susceptibility**,  $\chi$  mass unit, of anhydrous cobalt chloride. The salt is paramagnetic. P. Théodoridès gave  $96.29 \times 10^{-6}$  when corrected for the diamagnetism of the  $\text{Cl}^-$  ions; and T. Ishiwara, and K. Honda and T. Ishiwara gave for a field-strength of 2000 grms.:

	-81.4°	-16.7°	15.0°	90.6°	157.3°	308.4°	527.2°	686.1°
$\chi \times 10^6$ . . . . .	151.1	108.9	95.3	72.9	60.4	43.5	30.3	24.7

Observations were also made by R. Mercier, L. A. Welo, S. S. Bhatnagar and A. N. Kapur, H. R. Woltjer and H. K. Onnes, and A. Chatillon. H. R. Woltjer extrapolated the curve and gave  $-253^\circ$  for the Curie point; P. Théodoridès,  $-225.8^\circ$ ; and T. Ishiwara, and K. Honda and T. Ishiwara,  $-240^\circ$ . The effect of field-strength was measured by H. R. Woltjer, M. Wien, and H. R. Woltjer and H. K. Onnes, who found the magnetization curve at low field-strength is converse towards the H-axis, and at high field-strengths, it is linear. Observations were also made by P. Théodoridès, and B. Cabrera. A. Cotton studied the magnetic dichroism.

A. Chatillon found that the hexahydrate is paramagnetic; and that the susceptibility at different temp. is:

	-79°	0°	15°	40°	135.2°	153.5°	183.5°	208.5°
$\chi \times 10^6$ . . . . .	59.58	43.85	41.75	38.68	30.55	29.23	27.166	25.73
	Solid				Molten			

There is an abrupt rise of about 10 per cent. at about  $55^\circ$ , when the hexahydrate changes into the dihydrate. The Curie point with the hexahydrate is about  $-260^\circ$ . W. Klemm and W. Schüth found the magnetic susceptibility at  $293^\circ \text{K.}$ ,  $493^\circ \text{K.}$ , and  $673^\circ \text{K.}$  to be, respectively,  $\chi \times 10^6 = 95, 52$ , and 37. S. Meyer observed no remanent magnetization; and G. Roasio found that the crystals grown in a magnetic field are orientied, so that the  $C$ -axes are in the direction of the lines of force; and D. Samuracas, that the crystallization of the salt in aq. soln. is accelerated in a magnetic field.

M. Faraday noted that aq. soln. of moderate concentration are paramagnetic; and A. Quartaroli showed that soln. with 8.596 grms. of  $\text{CoCl}_2$  per litre, are

non-magnetic, and with greater dilutions, the diamagnetism of the water predominates. O. Liebknecht and A. P. Wills gave  $81 \times 10^{-6}$  mass unit for the magnetic susceptibility of soln. of cobalt chloride; G. Quincke,  $101 \times 10^{-6}$  at  $18^\circ$  to  $22^\circ$ ; G. Jäger and S. Meyer,  $81.5 \times 10^{-6}$  at  $18^\circ$ ; and G. Falckenberg,  $79.4 \times 10^{-6}$ . Observations were also made by L. Brant, S. Datta, G. Falckenberg and R. Oppermann, H. Fahlenbrach, G. Föex, A. Lallemand, P. Pascal, P. Vaillant, G. Wiedemann, and E. C. Wiersma. According to A. Chatillon, the sp. magnetic susceptibility of a 19.94 per cent. soln. of cobalt chloride is  $\chi_{\text{soln.}}$  mass unit, and the calculated value for the contained  $\text{CoCl}_2$  is  $\chi$ :

	$12.8^\circ$	$33.6^\circ$	$61.3^\circ$	$99.8^\circ$	$116.1^\circ$	$135.6^\circ$
$\chi_{\text{soln.}} \times 10^{-6}$	15.734	14.650	13.428	12.027	11.514	10.941
$\chi \times 10^{-6}$	81.80	76.35	70.23	63.20	60.63	57.81

B. Cabrera and co-workers found with  $C$  grms. of  $\text{CoCl}_2$  per gram of soln., the mol. susceptibility at about  $22^\circ$  to  $23^\circ$ :

$C$	0.3206	0.04903	0.02905	0.01095	0.00628	0.00525
$\chi_{\text{mol.}} \times 10^{-6}$	10,141	10,163	10,263	10,374	10,191	10,026

A. E. Oxley gave for soln. with  $C$  grm. of  $\text{CoCl}_2$  per c.c. at  $17.4^\circ$  the vol. susceptibility,  $\kappa$  vol. unit:

$C$	0.00622	0.00465	0.00311	0.00207	0.00155	0.00039
$\kappa \times 10^{-6}$	-0.251	-0.370	-0.500	-0.630	-0.630	-0.772

G. Wiedemann, G. Quincke, and G. Jäger and S. Meyer studied the influence of temp. on the susceptibility. The observations of L. Brant, G. Falckenberg and R. Oppermann, G. Jäger and S. Meyer, and A. E. Oxley show that the variation of the susceptibility with the conc. is linear; B. Cabrera and co-workers observed an increase with dilution up to a maxima with 0.00931 grm. per c.c., and then a decrease. P. Vaillant, and A. Quartaroli also noted a deviation from the linear relation. A. Trümpler, and A. Lallemand observed that the magnetic susceptibility of soln. of cobaltous chloride varies with concentration, and that the Curie points for concentration 0.072 to 0.0125 grm. of  $\text{CoCl}_2$  per gram of soln. rise from  $-18^\circ$  to  $-7^\circ$ . A. Chatillon found that the ageing of the soln. altered the susceptibility, but not so with A. Trümpler, and P. Weiss. B. Cabrera and co-workers observed that soln. prepared in the cold give different values from soln. prepared hot. P. Vaillant, and B. Cabrera and co-workers attributed the increase of susceptibility with dilution to the increasing ionization. A. Chatillon suggested that the change is due to an unstable magnetic state of the cobalt ions, and that the stable state is acquired only after the lapse of some 5 months. G. Quincke's statement that the susceptibility depends on the field-strength is, according to H. E. J. G. du Bois, based on an experimental error. G. Jäger and S. Meyer observed that the susceptibility is independent of the field-strength between 10,000 and 18,000 gauss; and L. Brant, between 3000 and 14,000 gauss for dil. soln., and 3000 and 10,000 gauss for conc. soln. P. Weiss, L. Brant, B. Cabrera and co-workers, A. Chatillon, G. Föex, A. Quartaroli, and P. Weiss and G. Föex discussed the magneton numbers; P. Pascal, A. E. Oxley, A. Chatillon, and B. Cabrera and co-workers studied the magnetic properties of soln. in hydrochloric acid; A. Quartaroli, in methyl alcohol; A. Quartaroli, and A. Chatillon, in ethyl alcohol; A. Chatillon, and W. Hardt, in normal amyl alcohol; A. Quartaroli, H. A. Curtis and R. M. Burns, and R. E. Wilson, in *iso*-amyl alcohol; and A. Quartaroli, in acetone. W. Sucksmith studied the gyromagnetic effect.

**Chemical properties of cobalt chloride.**—W. Spring observed that moist hydrogen reduces the red-hot chloride to metal; dry hydrogen does not reduce the chloride so readily, and there is then a partial sublimation of cobalt chloride—*vide supra*, the preparation of cobalt. F. de Carli compared the reducibility of the chloride with that of other metal chlorides. K. F. Bonhoeffer did not detect the reduction of cobaltous chloride by activated hydrogen. K. Jellinek and R. Uloth observed that at atm. press., the values for  $K = P_{\text{HCl}}/P_{\text{H}_2}$  at  $400^\circ$ ,  $500^\circ$ ,

and 600°, are, respectively, 0.110, 0.800, and 4.40. G. Crut found that the reaction with hydrogen is reversible:  $\text{CoCl}_2 + \text{H}_2 \rightleftharpoons \text{Co} + 2\text{HCl}$ , and the equilibrium constant,  $K = Q/4.571T + \log p + \log [\text{HCl}]^2/[\text{H}_2]$ , where  $p$  is the equilibrium pressure, and  $Q$  the heat of reaction, which is 32.0 cal. at 15°. At 445°,  $K = 10.9$ . J. H. Weibel studied the reaction. S. Miyamoto noted the chloride is reduced by hydrogen in the silent discharge. According to L. R. von Fellenberg, anhydrous cobalt chloride turns red a few minutes after exposure to **air**, owing to the absorption of moisture and the consequent formation of red hexahydrate. It is not affected by dry air. The blue hydrates also become red on exposure to air, and pass into the red hexahydrates. The red hexahydrates do not deliquesce on exposure to air. A. L. Potilitzin suggested that the cobaltous chloride in moist air passes first into the dihydrate, and more slowly into the hexahydrate; and F. W. O. de Coninck, that the tetrahydrate is formed at an intermediate stage in the hydration. J. Bersch said that the hexahydrate is stable in moist air; and A. L. Potilitzin, that it does not lose water in air at ordinary temp.; P. Sabatier, and J. C. G. de Marignac, that it deliquesces in moist air. A. L. Potilitzin found the dihydrate and the monohydrate are very hygroscopic. A. Ditte said that the crystals of the monohydrate become cloudy on exposure to air and break up into a rose-red powder. W. N. Hartley studied the deliquescence of the salt; and M. A. Razukin, the efflorescence of the hydrates. H. Schulze observed that when calcined in **oxygen**, or in air, black, crystalline cobaltous chloride is formed. H. Lescœur said that the formation of a basic chloride begins below 180°. K. Jellinek and A. Rudat observed that the action of oxygen on cobaltous chloride furnishes cobaltous oxide free from chlorine:  $3\text{CoCl}_2 + 2\text{O}_2 \rightleftharpoons \text{Co}_3\text{O}_4 + 3\text{Cl}_2$ . The vol. percentages of chlorine obtained at different temp. are:

	300°	350°	400°	500°	600°
$\text{Cl}_2$ . . . . .	1.12	1.0	1.9	11.3	47.0 per cent. by vol.

A. Mailfert studied the action of **ozone**. Anhydrous cobalt chloride dissolves in **water** very slowly, but, as indicated above, the chloride which has been exposed to air quickly dissolves in water. Observations on the solubility of the salt in water were made by R. Engel, A. Ditte, L. R. von Fellenberg, D. N. Bhattacharyya and N. R. Dhar, C. F. Bucholz, P. Sabatier, B. Franz, W. Stortenbeker, J. Bersch, etc. A. Étard found for the percentage solubility:

	-20°	-10°	0°	10°	20°	40°	50°	60°	80°	100°	120°
$S$ . . . . .	25.1	27.0	28.8	31.0	33.3	39.4	48.3	48.4	49.0	50.7	53.5
	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$						$\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$				

The cryohydrates and eutectics have been previously discussed. The corresponding solubility curve is shown in Fig. 78. A. L. Potilitzin gave 50° for the transition point  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O} \rightleftharpoons \text{CoCl}_2 \cdot 2\text{H}_2\text{O} + 4\text{H}_2\text{O}$ ; A. Chatillon gave 55°; and I. H. Derby and V. Yngve, 52.25°. H. W. Foote found that a sat. soln. of the hexahydrate at 0° has 31.66 per cent. of  $\text{CoCl}_2$ , and at 25°, 35.67 per cent.; C. Mazzetti gave 34.98 per cent. at 20°, and 51.93 per cent. at 98°; A. Benrath gave 34.86 per cent. at 20°, and 36.30 per cent. at 25°; and Y. Osaka and T. Yaginuma, 36.08 per cent. at 25°. W. W. Lucasse and H. J. Abrahams studied the action of the solvents glycol, pyridine, and methyl alcohol on the transition points.

The observations of H. G. Denham, R. Brdicka, and C. Kullgren on the hydrolysis of the chloride in aq. soln. have been already discussed. Basic salts have been reported. J. Habermann dropped dil. aq. ammonia into a boiling soln. of neutral cobalt chloride and obtained a peach-red precipitate of **cobalt hexahydroxydichloride**,  $3\text{Co}(\text{OH})_2 \cdot \text{CoCl}_2$  or  $\text{Co}_2(\text{OH})_3\text{Cl}$ , which, after drying, was rather hygroscopic but sparingly soluble

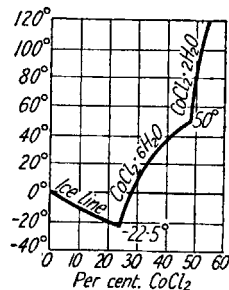


FIG. 78.—The Solubility Curve of Cobaltous Chloride.

in water. W. Feitknecht said that the X-radiograms show that the lattice contains alternate layers of hydroxide and normal salt. J. C. Duff and E. J. Bills obtained the salt by the action of hexamethylene tetramine on a soln. of cobaltous chloride. E. Hayek obtained **cobalt hydroxychloride**,  $\text{Co}(\text{OH})\text{Cl}$ . W. Meigen prepared the *pentahydrate*,  $3\text{Co}(\text{OH})_2 \cdot \text{CoCl}_2 \cdot 5\text{H}_2\text{O}$ , by the prolonged action of calcite or aragonite on a soln. of cobalt chloride. A. Werner discussed the constitution of this salt. C. W. Stillwell obtained a salt with a definite X-radiogram by treating an excess of a soln. of cobalt chloride with potash-lye, and allowing the mixture to stand some time. A. L. Potilitzin obtained a basic chloride by heating the hydrated chloride in air at  $100^\circ$  to  $120^\circ$ , and H. Lescœur, at  $120^\circ$ ; and F. Reitzenstein obtained **cobalt oxydichloride**,  $\text{CoO} \cdot \text{CoCl}_2$ , by heating  $\text{CoCl}_2 \cdot \text{C}_5\text{H}_5\text{N} \cdot \text{C}_5\text{H}_6\text{Cl}$  in an air-bath at  $150^\circ$ . F. Reiff described the oxychloride  $[\text{CoCl}_2(\text{H}_2\text{O})(\text{HO})]\text{H} \cdot \text{C}_4\text{H}_8\text{O}_2$ . According to A. Bernardi, with cold, dil. soln. of cobaltous chloride and sodium hydroxide, a blue basic salt is precipitated which soon turns green. The formation of the green salt depends on the proportions of the cobaltous salt and sodium hydroxide, and is formed only when the mol. ratio  $\text{NaOH} : \text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  is between the limits 0.02 to 0.44. The phenomenon depends on the formation of an oxidation product. A. C. Robertson, and A. von Kiss and F. E. Lederer studied the catalytic decomposition of **hydrogen dioxide** by cobalt chloride.

O. Ruff observed that **fluorine** at ordinary temp. converts the chloride into fluoride; A. Classen and B. Zahorsky, that liquid **chlorine** has no action on the anhydrous chloride; and A. L. Potilitzin, that when the chloride is heated with an equivalent of **bromine** in a sealed tube at  $400^\circ$ , approximately 3.82 per cent. of chlorine is displaced. R. Weinland and F. Schlegelmilch prepared orange-red crystals of hydrated **cobaltous bisiodotrichloro-chloride**,  $\text{CoCl}_2 \cdot 2\text{ICl}_3 \cdot 8\text{H}_2\text{O}$ , by the action of **iodine trichloride** on a soln. of cobalt chloride. C. Poulenc found that cobalt chloride is decomposed by **hydrogen fluoride** at room temp., and G. Gore said that the salt is insoluble in liquid hydrogen fluoride. A. Ditté reported that when **hydrogen chloride** is passed into conc. soln. of cobalt chloride, the monohydrate or the hemitrihydrate (*q.v.*) may be formed. R. Engel said that the dihydrate is converted into the anhydrous salt by hydrogen chloride at ordinary temp. N. Isgarischeff, and S. Schapiro studied the accelerating action of the chloride when **hydrochloric acid** acts on marble. P. Sabatier found that with increasing proportions of hydrochloric acid in aq. soln., the solubility of cobalt chloride first decreases and then increases. Expressing solubilities in eq. of acid and salt per 100 eq. of water, he found, at  $19^\circ$ :

HCl . . . . .	0	1.99	9.16	12.41	16.24
$\text{CoCl}_2$ . . . . .	7.777	6.13	3.29	4.57	4.70
Sp. gr. . . . .	1.397	1.307	1.256	1.290	1.314

The last soln. evolves hydrogen chloride when exposed to air, and deposits amethyst-blue needles of a lower hydrate, and when cooled it deposited a blue, granular precipitate which decomposed so readily that it could not be analyzed. It was thought to be a **cobalt hydrochloride**. R. Engel also obtained blue, deliquescent crystals of what was thought to be a hydrochloride, by cooling to  $-23^\circ$  a soln. saturated with hydrogen chloride and cobalt chloride. He thought that the unstable product might be  $\text{CoCl}_2 \cdot \text{HCl} \cdot 2(\text{or } 3)\text{H}_2\text{O}$ . H. W. Foote studied the ternary system:  $\text{CoCl}_2\text{-HCl-H}_2\text{O}$  at  $0^\circ$ , and found that only the hexa- and dihydrates were present as stable solid phases. There was no evidence of the formation of a hydrochloride. Expressing concentrations in grams per 100 grms. of sat. soln. at  $0^\circ$ , he found:

$\text{CoCl}_2$ . . . . .	31.66	25.58	5.97	2.69	11.58	12.42	12.66	15.12
HCl . . . . .	0.00	3.26	19.01	25.66	28.97	29.84	30.27	33.86
Solid phase	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$				$\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$			

The results are plotted in Fig. 79. H. Bassett and H. H. Croucher were unable to obtain any compound with hydrogen chloride, even at temp. down to  $-20^{\circ}$  with soln. sat. with the gas at atm. press., though with higher gas pressures a compound of the type  $\text{CoCl}_2 \cdot \text{HCl} \cdot 3\text{H}_2\text{O}$  might be formed, analogous with the lithium salt of A. Chassevant,  $\text{CoCl}_2 \cdot \text{LiCl} \cdot 3\text{H}_2\text{O}$ , and in accord with the work of F. G. Donnan and H. Bassett on the complex anions in soln.—*vide supra*—the lithium salt might be  $[\text{Li}(\text{H}_2\text{O})_2][\text{Co}(\text{H}_2\text{O})\text{Cl}_3]'$ , which would agree with the further assumption that the blue anion is  $[\text{Co}(\text{H}_2\text{O})\text{Cl}_3]'$ . H. Bassett and H. H. Croucher found at  $25^{\circ}$ :

$\text{CoCl}_2$	35.87	28.54	12.77	15.50	18.50	18.18	17.55	21.00
$\text{HCl}$	0.00	5.29	20.50	22.51	22.85	23.45	26.72	31.10

Solid phase

 $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ 

They represent the hexahydrate,  $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_2$ , and the dihydrate,  $[\text{Co}(\text{H}_2\text{O})_4]\text{CoCl}_4$ . R. Engel, and J. Kendall and K. P. Monroe measured the sp. gr. of hydrochloric acid soln. of cobaltous chloride; O. R. Howell, J. Kendall and K. P. Monroe, and N. A. Yajnik and R. L. Uberoy, the viscosity; E. Rona, the diffusion; O. R. Howell, the surface tension, and the indices of refraction; G. J. Elias, the magnetic rotation of the plane of polarization; W. R. Brode, G. Denigès, R. Engel, and O. R. Howell, the colour, and absorption spectrum; F. G. Donnan and H. Bassett, and H. Bassett and H. H. Croucher, the constitution of the soln.; O. R. Howell, the electrical conductivity; A. E. Oxley, P. Pascal, A. Chatillon, and B. Cabrera and co-workers, the magnetic properties; and B. Cabrera and co-workers, and A. Chatillon, the magneton numbers.

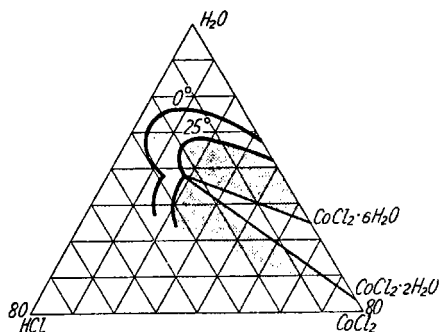


FIG. 79.—Ternary System:  $\text{CoCl}_2$ - $\text{HCl}$ - $\text{H}_2\text{O}$ , at  $0^{\circ}$  and  $25^{\circ}$ .

According to A. J. Balard, and E. and B. Klimenko, anhydrous cobalt chloride with **hydrochlorous acid** gives a precipitate of hydrated cobaltic oxide, and chlorine is evolved. A. W. Ralston and J. A. Wilkinson, W. Biltz, and E. Keunecke found that anhydrous cobalt chloride is insoluble in liquid **hydrogen sulphide**. J. Myers said that when cobalt chloride is heated with **potassium sulphide**, cobalt, and alkali polysulphide are formed. C. Dufraisse and D. Nakae studied the effect on the oxidation of a soln. of **sodium sulphite**. H. L. Haken studied the action of **hyposulphites** on cobalt salt soln. A. Vogel observed that when cobalt chloride is treated with **sulphuric acid**, oxygen is evolved even in the cold. F. Ephraim said that with conc. sulphuric acid, hydrogen chloride is evolved at ordinary temp. A. Hantzsch and H. Carlsohn studied the action of dil. sulphuric acid. F. J. Faktor observed that when triturated with **sodium thiosulphate**, cobaltous chloride becomes green, and when the mixture is heated, molten sodium cobalt sulphide,  $\text{Na}_2\text{Co}_4\text{S}_6$ , is formed. C. R. Wise found that 100 grms. of a sat. soln. in **selenium oxychloride** contain 0.17 grm. of  $\text{CoCl}_2$  at  $25^{\circ}$ .

G. Gore, and E. C. Franklin and C. A. Kraus noted that anhydrous cobalt chloride is insoluble in liquid **ammonia**; and E. Divers, that it swells up in a soln. of ammonium nitrate in ammonia. T. Vorster observed that when cobalt chloride is heated in ammonia gas, it is reduced to metal, but H. Rose, and F. Rose, etc., observed that at ordinary temp. the anhydrous chloride absorbs ammonia gas, producing a voluminous, pale pink powder of an ammine. The existence of four aminochlorides have been definitely established—the deca-, hexa-, and di-, and mono- amines—and G. L. Clark and co-workers announced a yellowish-red **cobaltous pentamminochloride**,  $\text{CoCl}_2 \cdot 5\text{NH}_3$ , of sp. gr. 1.580, to be formed by passing ammonia into a soln. of cobalt chloride in absolute alcohol; a rose-red



**cobaltous aquopentamminochloride**,  $\text{CoCl}_2 \cdot 5\text{NH}_3 \cdot \text{H}_2\text{O}$ , of sp. gr. 1.559, by passing ammonia into an aq. soln. of cobalt chloride at  $-10^\circ$ ; and a **cobaltous tetramminochloride**,  $\text{CoCl}_2 \cdot 4\text{NH}_3$ , of sp. gr. 1.593, by H. Rose, by passing ammonia over dry cobalt chloride, and by G. L. Clark and co-workers, by keeping the hexammine in vacuo at room temp., or over sulphuric acid at  $50^\circ$  for 36 hrs., or by heating the

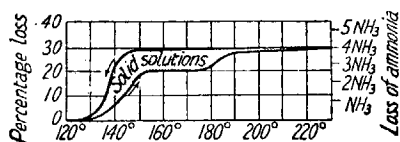


FIG. 80.—The Heating and Cooling Curves of Cobaltous Hexamminochloride.

the anhydrous chloride respectively in ammonia at 1 atm. press. is indicated in Fig. 80. The irreversibility of the composition-temperature curves in the region between the diammine and the hexammine is taken to be the result of the formation of solid soln. by the decomposing hexammine. The co-ordination and structure were discussed by P. C. Ray.

G. L. Clark and co-workers obtained **cobaltous decamminochloride**,  $\text{CoCl}_2 \cdot 10\text{NH}_3$ , by the action of ammonia gas on flocculent cobaltous chloride at a low temp. The brown product has a sp. gr. of 1.71, and on standing it passes into the hexammine. This may be the same as the pale rose-red decammine prepared by W. Biltz and C. Messerknecht. The crystalline hexammine takes up very little ammonia under the same conditions. W. Biltz found the dissociation press. of the decammine to be 25.5 mm. at  $-78.5^\circ$ , 56.0 mm. at  $-70^\circ$ , 87.0 mm. at  $-65^\circ$ , 131.5 mm. at  $-60^\circ$ , and 190 mm. at  $-55^\circ$ . The heat of formation from the hexammine is 7.20 Cals. per mol. of  $\text{NH}_3$ , and from  $\text{CoCl}_2$ , 12.02 Cals. per mol. of ammonia.

E. Frémy prepared **cobaltous hexamminochloride**,  $\text{CoCl}_2 \cdot 6\text{NH}_3$ , by dissolving the greenish-blue precipitate produced by ammonia on conc. soln. of cobalt chloride in an excess of ammonia, and with the exclusion of air. The soln. furnishes pale rose-red octahedra of the hexammine. F. Rose recommended pouring the conc. soln. of cobalt chloride into conc. aq. ammonia, dissolving the precipitate by heating the soln., and allowing the filtered soln. to stand for some hours, when crystals of the hexammine are formed. A. Naumann and J. Rill obtained the salt in an analogous manner, and also by passing dry ammonia into a soln. of cobalt chloride in methyl acetate. A. Naumann and E. Vogt used acetone as solvent; and G. L. Clark and co-workers, and W. Biltz and B. Fetkenheuer, alcohol. J. Bersch,

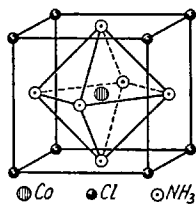


FIG. 81.—The Arrangement of Atoms about Each Cobalt Atom of Cobaltous Hexamminochloride.

W. Peters, F. Ephraim, and W. Biltz and B. Fetkenheuer obtained the hexammine by passing ammonia over dry cobalt chloride. The octahedral crystals vary from flesh-red to red, according to the mode of preparation; P. Stoll found that the X-radiograms corresponded with a cubic lattice of the calcium fluoride type. The lattice parameter  $a=9.87\text{Å}$ . There are 4 mols. in the elementary cell. The cobalt atoms are located at the corners and the centres of the faces of a cube. Each cobalt atom is surrounded by six  $\text{NH}_3$ -groups arranged at the corners of an octahedron, the cobalt atoms are at the corners of an octahedron, and the chlorine atoms at the corners of a cube. W. Biltz and E. Birk gave  $a=10.12\text{Å}$ ; and G. B. Naess and O. Hassel, 10.10 Å., and 4.37 Å. for the distance between the Co and Cl atoms. The arrangement about each cobalt atom is shown in Fig. 81. G. L. Clark and co-workers found the sp. gr. to be 1.497 at  $25^\circ/4^\circ$ , and W. Biltz and co-workers

gave 1.479 at  $25^{\circ}/4^{\circ}$ ; mol. vol., 156.9; mol. vol. of each of the six ammonia mols., 19.67. G. Beck studied the subject. The decomposition of the salt prevents a determination of the m.p. The dissociation press.,  $p$  mm., is:

	82.5°	92.5°	101.5°	111.0°	118°	126°	132°	136°	139.5°
$p$	75	101	156	231	305	425	538	620	703

These results by F. Ephraim are considered by W. Biltz and B. Fetkenheuer to be too low. W. Biltz gave the results summarized in Fig. 82, for the stability ranges of the amines. W. Peters also made some observations on the subject. F. Ephraim measured the dissociation press. of mixtures of cobalt and nickel hexamminochlorides. G. Beck gave 323 cal. for the heat of formation. W. Biltz and B. Fetkenheuer calculated the heat of formation of the hexamine from the diamminochloride to be 14.5 Cals. per mol. of  $\text{NH}_3$ ; and W. Biltz and G. F. Hüttig, 12.9 Cals. per mol. of  $\text{NH}_3$ ; and W. Biltz obtained nearly 15.5

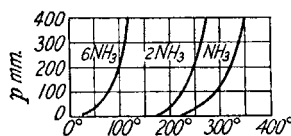


FIG. 82.—Dissociation Pressures of the Cobaltous Diamminochlorides.

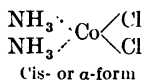
Cals. per mol. of  $\text{NH}_3$  for the heat of formation from cobalt chloride and ammonia. L. Pauling and M. L. Huggins investigated the magnetic properties. The subject was studied by G. L. Clark, H. von Sanden, W. Hieber and E. Levy, and W. Hieber and F. Mühlbauer. A. B. Lamb and A. T. Larson found the equilibrium constant for the ionization:  $[\text{Co}(\text{NH}_3)_6]^{++} \rightleftharpoons \text{Co}^{++} + 6(\text{NH}_3)$  is  $1.25 \times 10^{-5}$ . F. Rose noted that the hexamine oxidizes when exposed to air, and particularly so if the hexamine is moist. W. Gluud and co-workers studied the oxidation of the hexamine. E. Frémy found that the hexamine is hydrolyzed by water, to form a green, basic salt, but it dissolves without decomposition in conc. aq. ammonia. F. Rose added that the salt is freely soluble in dil. aq. ammonia, less soluble in conc. aq. ammonia, and insoluble in alcohol. N. S. Kurnakoff observed that a complex salt is formed with platinous chloride,  $\text{Co}(\text{NH}_3)_6\text{Cl}_2 \cdot \text{PtCl}_2$ .

F. Rose prepared **cobaltous diamminochloride**,  $\text{CoCl}_2 \cdot 2\text{NH}_3$ , by heating the hexamine to  $120^{\circ}$ ; G. L. Clark and co-workers, and W. Biltz and B. Fetkenheuer, by exposing the hexamine in vacuo over conc. sulphuric acid, at  $65^{\circ}$  to  $67^{\circ}$ ; A. Naumann and E. Vogt, by passing ammonia into a soln. of cobalt chloride in acetone, or, according to A. Naumann and J. Rill, into a soln. of the chloride in methyl acetate. There are two forms of the diammine. The bluish-violet one just indicated is the *unstable* or  $\beta$ -form, or the *trans*-form. The rose-red salt—the *stable* or  $\alpha$ -form or the *cis*-form—was obtained by W. Biltz and B. Fetkenheuer by passing dry ammonia over the hexamine at about  $137^{\circ}$ ; and by G. L. Clark and co-workers by passing dry ammonia into a boiling soln. of cobalt chloride in dry amyl alcohol. According to G. L. Clark and co-workers, the pale rose-red product has a sp. gr. of 2.097 at  $25^{\circ}/4^{\circ}$ , a mol. vol. of 78.25, and the mol. vol. of the ammonia is 19.77. W. Biltz and B. Fetkenheuer gave  $273^{\circ}$  for the m.p., and for the dissociation press.,  $p$  mm.:

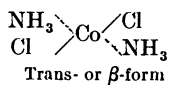
	136.5°	153.5°	168.0°	183.5°	230°	234°	236°
$p$	6.9	13.3	27.0	42.5	82.4	85.2	89.9

The heat of formation from the monamine, calculated by W. Biltz and B. Fetkenheuer, is 18.67 Cals., and from cobalt chloride, it is 19.88 Cals. per mol. of  $\text{NH}_3$ . The subject was discussed by G. L. Clark, and W. Hieber and E. Levy. W. Biltz found that the sp. magnetic susceptibility of the  $\alpha$ -form is  $76 \times 10^{-6}$  mass unit, and of the  $\beta$ -form,  $74 \times 10^{-6}$  mass unit. When the  $\beta$ -form is heated to  $210^{\circ}$  in dry ammonia, it passes into the  $\alpha$ -form; the dissociation press. of the  $\beta$ -form at  $216^{\circ}$  is 14.5 mm. lower than that of the  $\alpha$ -form. The  $\alpha$ -form is rose-pink, the  $\beta$ -form is blue. The  $\beta$ -form is more sensitive than the  $\alpha$ -form to water, and water vapour. W. Klemm and W. Schüth studied the magnetic susceptibility. The structure was discussed by A. Hantzsch. W. Biltz and B. Fetkenheuer assume

that the  $\alpha$ -form is cobaltous cis-diamminochloride, and the  $\beta$ -form is cobaltous trans-diamminochloride :



(cis- or  $\alpha$ -form)



Trans- or  $\beta$ -form

G. L. Clark and co-workers heated a mixture of cobalt chloride and its hexammine in theoretical proportions in a sealed tube at  $230^\circ$ , and obtained **cobaltous monamminochloride**,  $\text{CoCl}_2 \cdot \text{NH}_3$ . W. Biltz and B. Fetkenheuer obtained it by heating the hexammine in vacuo at  $230^\circ$ . The violet-blue powder melts at  $321^\circ$ , its dissociation press. at  $208^\circ$ ,  $215^\circ$ , and  $210^\circ$  are, respectively, 2.86, 3.76, and 8.05 mm. The heat of formation from ammonia and cobalt chloride is about 21.2 Cals.

F. W. Bergstrom observed that no definite product is formed by the action of **potassium amide** on a soln. of cobaltous chloride in liquid ammonia. T. W. B. Welsh and H. J. Broderson found that 100 grms. of anhydrous **hydrazine** dissolve about a gram of anhydrous cobalt chloride at about  $15^\circ$ ; and C. Paal and L. Friederici observed no reduction at  $100^\circ$ . H. Franzen and O. von Mayer prepared **cobaltous dihydrazinochloride**,  $\text{CoCl}_2 \cdot 2\text{N}_2\text{H}_4$ , by heating a mixture of cobaltic chloropentamminochloride, hexamminochloride, or aquopentamminochloride and 50 per cent. hydrazine hydrate on a water-bath. T. Curtius and L. Guttman obtained the complex salt by treating a soln. of thoroughly dried cobalt chloride in absolute alcohol with anhydrous hydrazine; or hydrazine hydrate. W. Hieber and co-workers studied the energy of formation. According to H. Franzen and O. von Mayer, the rose-red powder is insoluble in cold water, but it is hydrolyzed by boiling water; it is soluble in dil. acids and in aq. ammonia; and when heated in an atm. of carbon dioxide, it forms anhydrous cobaltous chloride. P. C. Ray and H. Bhar found the magnetic susceptibility to be  $48.7 \times 10^{-6}$  mass unit; and D. M. Bose discussed the magnetic properties of the complex salts. A. Ferratini obtained **cobaltous pentahydrazinooctochloride**,  $2\text{CoCl}_2 \cdot 4\text{N}_2\text{H}_5\text{Cl} \cdot \text{N}_2\text{H}_4$ , by mixing an aq. soln. of the components, and boiling the product with 94 per cent. alcohol. The violet crystals of the required salt are separated mechanically from the wine-red crystals. The salt melts between  $221^\circ$  and  $223^\circ$ , it is easily soluble in water, and aq. alcohol. He also prepared **cobaltous dihydrazinotetrachloride**,  $\text{CoCl}_2 \cdot 2\text{N}_2\text{H}_5\text{Cl} \cdot 2\frac{1}{2}\text{H}_2\text{O}$ , in wine-red crystals melting at  $213^\circ$  to  $215^\circ$  with decomposition. Complex salts with **phenylhydrazine** were obtained by J. Moitessier, J. Ville and J. Moitessier, and W. Hieber and co-workers. W. Feldt prepared **cobaltous dihydroxylamino-chloride**,  $\text{CoCl}_2 \cdot 2\text{NH}_2\text{OH}$ , by adding hydroxylamine hydrochloride, and an alcoholic soln. of hydroxylamine to a boiling aq. soln. of cobalt chloride. The salt which separates out is washed with alcohol, and ether. It is rose-red; stable when protected from air; and detonates when heated. H. Rose observed that when cobalt chloride is heated with **phosphorus**, cobalt phosphide, and phosphorus trichloride are formed; the salt is easily decomposed by **phosphine**. O. J. Walker observed that in ammoniacal soln., a stick of phosphorus precipitates cobalt phosphide. H. L. Haken, R. Scholder and co-workers, and C. Paal and L. Friederici found that an **alkali hypophosphite** precipitates a mixture of cobalt and cobalt phosphide. F. Fleissner, and R. H. Pickard and J. Kenyon obtained compounds with the **phosphine oxides**—e.g., with **triphenyl phosphine oxide** there is formed  $\text{CoCl}_2 \cdot 2(\text{C}_6\text{H}_5)_3\text{PO}$ .

J. H. Weibel studied the action of **carbon monoxide**. S. von Laszczynsky studied the action of **benzene** on cobaltous chloride. W. J. Russell said that cobaltous chloride is insoluble in **carbon tetrachloride**; but it is readily dissolved by **ethyl chloride**. F. Schlegel, and A. Hantzsch and F. Schlegel obtained the complex  $\text{CoCl}_2 \cdot 6\text{CH}_3\text{OH}$ , by cooling conc. soln. of cobaltous chloride in **methyl alcohol** to  $-20^\circ$ . The pale red crystals melt to a blue liquid at ordinary temp., and lose all their alcohol at  $130^\circ$ . E. Lloyd and co-workers found that the complex

$\text{CoCl}_2 \cdot 3\text{CH}_3\text{OH}$  separates from a soln. at  $37^\circ$ , and its vap. press. at  $20^\circ$  is 29.4 mm., and at  $35^\circ$ , 81.9 mm. The solubility of cobalt chloride in methyl alcohol,  $S$  grm.  $\text{CoCl}_2$  per gram of solvent is :

$S$	$20^\circ$	$25^\circ$	$30^\circ$	$35^\circ$	$37.1^\circ$	$38^\circ$	$40^\circ$	$50^\circ$
	0.385	0.436	0.488	0.555	0.589	0.588	0.582	0.589
	$\text{CoCl}_2 \cdot 3\text{CH}_3\text{OH}$					$\text{CoCl}_2 \cdot 2\text{CH}_3\text{OH}$		

The transition temp. is  $37.10$ . The blue crystals of  $\text{CoCl}_2 \cdot 2\text{CH}_3\text{OH}$  were obtained by A. Benrath by evaporating the soln. over sulphuric acid. E. Toporescu found that the blue soln. becomes red at  $3^\circ$ . M. R. Schmidt and H. C. Jones measured the viscosity of soln. of cobalt chloride in methyl alcohol, and in mixtures of methyl alcohol and glycerol; and R. Salvadori, and O. E. Frivold, the mol. lowering of the b.p. The colour and absorption spectrum were discussed by F. L. Cooper, H. A. Curtis and R. M. Burns, J. Groh and R. Schmidt, A. Hantzsch and co-workers, E. O. Hulbert and co-workers, H. C. Jones and co-workers, J. Lifschütz and E. Rosenbohm, C. Mazzetti, W. J. Russell, and E. Toporescu. According to F. Schlegel, solutions of cobalt halides in ethyl, amyl, and benzyl alcohols, glacial acetic acid, ethyl acetate, ethyl formate, acetone, acid amides, and nitriles are blue; and those in water, methyl alcohol, glycerol, glycol, and pyridine are rose-red. The electrical conductivity of the soln. was studied by H. C. Jones and L. McMaster, W. Hardt, H. R. Kreider and H. C. Jones, E. Rimbach and K. Weitzel, and M. R. Schmidt and H. C. Jones; the degree of ionization, by W. Hardt, H. R. Kreider and H. C. Jones, and R. Salvadori; and the magnetic properties by A. Quartaroli.

C. Winkler observed that anhydrous cobalt chloride is soluble in **ethyl alcohol**, and a sat. soln. in alcohol of sp. gr. 0.792 contains 23.66 per cent. of cobalt chloride, and has a sp. gr. of 1.0107. The soln. is blue by transmitted light, and black by reflected light. A 1 : 2500 soln. is distinctly blue, but a 1 : 10,000 soln. is colourless when cold, and blue when hot. Water added to the blue alcoholic soln. turns it violet and then red. Hence, the blue soln. can be used to detect the presence of water. E. Toporescu found that the blue soln. becomes red at  $-18^\circ$ . The alcoholic soln. was also studied by E. Bödtker, and F. Bourion. S. von Laszczynsky found that 100 grms. of absolute alcohol can dissolve 56.2 grms. of cobalt chloride at room temp., and the addition of water precipitates hexahydrated cobalt chloride from the alcoholic soln. H. Ditz said that the blue soln. in 96 per cent. alcohol becomes red when it is mixed with water, and that the blue colour is restored by ether or absolute alcohol. R. Engel suggested that the blue soln. contains a blue alcoholate, and E. Bödtker assumed that the hexahydrate in alcoholic soln. decomposes into  $\text{CoCl}_2 \cdot 5\text{H}_2\text{O} + \text{H}_2\text{O}$ , and in dil. soln. the water is present as  $\text{H}_2\text{O}$ -mols., and in conc. soln. as  $(\text{H}_2\text{O})_2$ -mols. E. Lloyd and co-workers found the solubility of cobalt chloride,  $S$  grm. of  $\text{CoCl}_2$  per gram of ethyl alcohol, to be :

$S$	$0^\circ$	$10^\circ$	$20^\circ$	$30^\circ$	$38^\circ$	$40^\circ$	$50^\circ$	$60^\circ$	$70^\circ$	$80^\circ$
	0.450	0.486	0.544	0.626	—	0.674	0.651	0.668	0.729	0.703
	$\text{CoCl}_2 \cdot 3\text{C}_2\text{H}_5\text{OH}$					$\text{CoCl}_2 \cdot 2\text{C}_2\text{H}_5\text{OH}$				

The complex  $\text{CoCl}_2 \cdot 3\text{C}_2\text{H}_5\text{OH}$  separates from the sat. soln. below the transition temp.,  $38^\circ$ ; and the vap. press. of the blue crystals is 0.85 mm. at  $10^\circ$ , and 5.54 mm. at  $30^\circ$ . When the alcoholic soln. is evaporated in vacuo over phosphorus pentoxide, it deposits the complex  $\text{CoCl}_2 \cdot 2\text{C}_2\text{H}_5\text{OH}$ ; the blue crystals are very deliquescent, and they lose all their alcohol at  $100^\circ$ . F. Bourion reported that the complex  $\text{CoCl}_2 \cdot 2\frac{1}{2}\text{C}_2\text{H}_5\text{OH}$  separates in blue, deliquescent needles by evaporating an alcoholic soln. of cobalt chloride. The heat of formation is said to be 3.03 Cals., and the sp. gr. 1.32 at  $22^\circ/4^\circ$ . N. Schiloff and S. Pewsner studied the adsorption of the salt by charcoal from soln. of the salt in mixtures of alcohol and water. M. R. Schmidt and H. C. Jones studied the viscosity of soln. in ethyl alcohol, and in mixtures of ethyl alcohol and glycerol; O. E. Frivold, and A. Benrath, the mol. raising of the

b.p.; and M. S. Wrewsky, the sp. ht. The colour and absorption spectrum was discussed by W. R. Brode, A. R. Brown, F. L. Cooper, F. G. Donnan and H. Bassett, J. Formanek, J. H. Gladstone, A. Hantzsch, W. Hardt, R. A. Houstoun and co-workers, H. C. Jones and co-workers, C. Mazzetti, A. Rosenheim and V. J. Meyer, W. J. Russell, Y. Shibata and T. Inoue, J. H. Smith, H. W. Vogel, B. Völlmer, and M. S. Wrewsky; and the magnetic rotation of the plane of polarization, by R. W. Roberts. The electrical conductivity of the alcoholic soln. was studied by W. Hardt, H. C. Jones and co-workers, H. R. Kreider and H. C. Jones, E. Rimbach and K. Weitzel, A. Rosenheim and V. J. Meyer, and M. R. Schmidt and H. C. Jones; and the magnetic properties, by A. Chatillon, L. Landau, and A. Quartaroli.

The soln. of cobalt chloride in normal **propyl alcohol** is blue at ordinary temp. It was studied by E. O. Hulbert and co-workers, and E. Toporescu found that the soln. becomes red at  $-32^{\circ}$ ; and in normal **butyl alcohol**, the blue soln. becomes red at  $-65^{\circ}$ . E. O. Hulbert and co-workers studied the blue soln. of cobalt chloride in **iso-butyl alcohol**. W. Hardt measured the electrical conductivity of soln. in normal **amyl alcohol**, and A. Chatillon, the magnetic properties; E. Toporescu found that the blue soln. becomes red at  $-65^{\circ}$ . The dark blue soln. of cobalt chloride in **iso-amyl alcohol** was studied by H. A. Curtis and R. M. Burns; the colour, and absorption spectrum, by E. O. Hulbert; the electrical conductivity, by R. E. Wilson; and the magnetic properties, by A. Quartaroli. H. A. Curtis and R. M. Burns observed that hydrogen sulphide only partially precipitates the cobalt from the soln. A. Hantzsch and F. Schlegel observed that the hot, blue soln. of the salt in **benzyl alcohol** deposits red crystals of the complex  $\text{CoCl}_2 \cdot 4\text{C}_7\text{H}_7\text{OH}$ . B. Köhnlein observed a slight reaction with **propyl iodide**.

F. W. O. de Coninck found that 100 grms. of a soln. in anhydrous **ethylene glycol** contain 10.6 of the hexahydrate at  $16.4^{\circ}$ . The soln. in glycol changes from purple to a bluish-violet when it is exposed to sunlight, and the purple soln. in glycol also becomes blue when heated. A. Hantzsch, and A. Grün and E. Boedecker prepared the blue complex  $\text{CoCl}_2 \cdot 3\text{C}_2\text{H}_4(\text{OH})_2$ , melting at  $68^{\circ}$ ; and A. Grün and E. Boedecker obtained the dihydrate and monohydrate, as well as the complex  $\text{CoCl}_2 \cdot 2\text{C}_2\text{H}_4(\text{OH})_2$ ; it also forms a complex with **propylene glycol**,  $\text{CoCl}_2 \cdot 3\text{C}_3\text{H}_6(\text{OH})_2$ ; and with **pinacone**,  $2\text{CoCl}_2 \cdot 3\text{C}_6\text{H}_{12}(\text{OH})_2$ . F. Guthrie observed that the soln. of cobaltous chloride in **glycerol** is carmine-red at ordinary temp., blue when heated, and yellowish when cooled by solid carbon dioxide. M. R. Schmidt and H. C. Jones, and H. C. Jones and J. S. Guy measured the viscosity, and the electrical conductivity of the soln.; and H. C. Jones and W. W. Strong, and W. J. Russell, the colour and absorption spectrum.

E. Bödtker observed that 100 grms. of **ether** dissolve 0.021 grm. of anhydrous cobalt chloride, and 0.291 grm. of the hexahydrate; and S. von Laszczynsky added that 100 grms. of ether dissolve 0.11 grm. of the dihydrate at  $11^{\circ}$  and  $35^{\circ}$ . F. N. Speller studied the partition of the chloride between ether and dil. hydrochloric acid. A. Hantzsch and H. Carlsohn, and W. J. Russell studied the colour and absorption spectrum of the soln. W. Eidman observed that cobaltous chloride is soluble in **acetone**. K. P. MacElroy and W. H. Krug observed that at  $25^{\circ}$ , 100 grms. of dry acetone dissolve 8.62 grms. of  $\text{CoCl}_2$ ; A. Naumann and E. Vogt, at  $18^{\circ}$ , 2.78 grms.; S. von Laszczynsky, at  $0^{\circ}$ , 9.11 grms., and at  $22.5^{\circ}$ , 9.28 grms. of  $\text{CoCl}_2$ , and 17.16 and 17.06 grms. of the dihydrate per 100 grms. of solvent, respectively, at  $0^{\circ}$  and  $25^{\circ}$ . W. R. G. Bell and co-workers found the solubility,  $S$  grms.  $\text{CoCl}_2$  per 100 grms. of acetone, to be:

	$0^{\circ}$	$10^{\circ}$	$20^{\circ}$	$22.5$	$25^{\circ}$	$30^{\circ}$	$40^{\circ}$	$50^{\circ}$
$S$	4.47	3.32	2.89	3.40	3.71	4.51	6.01	7.25

where below  $19.5^{\circ}$ , the solid phase is  $\text{CoCl}_2 \cdot \text{C}_3\text{H}_6\text{O}$ , and above that temp.,  $\text{CoCl}_2$ . A. Naumann and E. Vogt found that the blue soln. turns green when it has stood for some time. The complex was prepared by S. von Laszczynsky, who found that it is stable at  $100^{\circ}$ , but W. R. G. Bell observed that the vap. press. at  $10^{\circ}$  is 103.6 mm.,

and at 15°, 125 mm. A. Naumann and E. Vogt found that the sp. gr. of a sat. soln. is 0.825 at 18°/4°. A. L. Robinson measured the mol. raising of the b.p. The colour and absorption spectrum were studied by J. Groh and R. Schmidt, R. A. Houstoun and co-workers, and H. C. Jones and co-workers; the electrical conductivity, by F. Bauer, H. C. Jones and L. McMaster, E. Rimbach and K. Weitzel, and M. Wien; the electrolysis of the soln., by J. E. Marsh; and the magnetic properties, by A. Quartaroli. According to A. Naumann and E. Vogt, the soln. gives a precipitate of silver chloride when it is treated with silver nitrate; a dark blue soln. when it is treated with potassium thiocyanate; and when treated with ammonia, it first forms the diamminochloride and afterwards the hexamminochloride. They also observed the action of bromine, iodine, and hydrogen chloride on the soln. E. Raymond studied the complex formed with **benzaldehyde**.

O. Aschan found that 100 grms. of 95 per cent **formic acid** dissolve 6.2 grms. of  $\text{CoCl}_2$  at 20.5°. A. W. Davidson found that the chloride is readily dissolved by **acetic acid**, and W. J. Russell added that the absorption spectrum resembles that of a dil. alcoholic soln. A. Naumann and J. Rill found that 100 grms. of **methyl acetate** dissolve 0.369 grm. of  $\text{CoCl}_2$  at 18°, and the soln. has a sp. gr. of 0.938 at 18°/4°. The blue soln. becomes red when treated with water. They also observed the action of potassium thiocyanate, lithium nitrate, and of ammonia on the soln. A. Naumann and E. Alexander found that cobalt chloride is sparingly soluble in **ethyl acetate**, and S. von Laszczynsky, that 100 grms. of solvent dissolve 0.08 grm. of  $\text{CoCl}_2$  at 14°, and 0.26 grm. at 79°, whilst the hexahydrate is insoluble in ethyl acetate. W. J. Russell found cobalt chloride is readily soluble in **amyl acetate**. S. Hakomori studied the action of **oxalic, citric, malic, and succinic acids** on cobalt chloride.

A. Naumann and A. Schier reported that 100 grms. of **acetonitrile**, at 18°, dissolve 4.08 grms. of  $\text{CoCl}_2$ . The blue soln. becomes a little turbid by hydrogen sulphide, and this is not cleared up by the action of hydrogen chloride. They reported that a complex,  $\text{CoCl}_2 \cdot 3\text{CH}_3\text{CN}$ , is formed in the soln.; A. Hantzsch, however, said that the formula of the complex is  $\text{CoCl}_2 \cdot 2\text{CH}_3\text{CN}$ . A. Hantzsch and F. Schlegel, and A. Naumann found that cobalt chloride is easily soluble in **benzonitrile**, forming a deep blue soln., and when the hot sat. soln. is cooled, A. Werner obtained blue needles of a complex. K. A. Hofmann and G. Bugge, and A. Hantzsch observed that a complex is formed with **ethyl carbylamine**,  $\text{CoCl}_2 \cdot 2\text{C}_2\text{H}_5\text{NC}$ . P. Pfeiffer and F. Tappermann prepared compounds with **triphenyl-** and **tri-phenanthroline**. Cobalt chloride forms complex salts with many amines, and their stability was discussed by F. Mühlbauer. It forms a complex salt or salts with **methylamine**, studied by F. Ephraim and R. Linn, and W. Hieber and co-workers; with **ethylamine**, by F. Ephraim and R. Linn, W. Hieber and co-workers, and F. L. Shinn; with **allylamine**, by E. Lippmann and G. Vortmann, E. G. V. Percival and W. Wardlaw, A. Pieroni, and A. Pinotti—*vide supra*, cobaltic chloride; J. Frejka and L. Zahlova, with **diaminobutane**; with **ethyldiammine**, by W. Hieber and A. Woerner, and N. S. Kurnakoff; and with **hexamethylene-tetramine**, by J. C. Duff and E. J. Bills, G. A. Barbieri and F. Calzolari, M. R. Menz, and G. Scagliarini and G. Tartarini. The complex with **thiourea** was studied by G. Walter, and A. Rosenheim and V. J. Meyer. P. Walden found that red soln. are formed with **formamide**; and H. Röhrer studied the electrolysis of the soln. A complex is formed with **acetamide**, which was studied by G. André, G. Bruni and A. Manuelli, and L. F. Yntema and L. F. Audrieth; with **urethane**, by N. Castoro, J. Beato and M. de los D. Brugger, and G. Bruni and A. Manuelli; with **aniline**, by A. R. Leeds, W. Hieber and E. Levy, S. von Laszczynsky, W. Hieber and A. Woerner, G. Reddelein, and E. Lippmann and G. Vortmann; with **methylaniline**, by J. Reilly; with **butylaniline**, by J. Reilly; with **toluidine**, by E. Lippmann and G. Vortmann, J. Beato and M. de los D. Brugger, and G. Spacu; with **xylylidine**, by E. Lippmann and G. Vortmann; with **ethylenediamine**, by W. Hieber and F. Mühlbauer, and O. Stelling; with **o-phenylenediamine**, by

W. Hieber and K. Ries; with **diphenylethylenediamine**, by J. V. Dubsky and A. Langer; with **phenylenediamine**, by W. Hieber and co-workers, R. Cernatescu and co-workers, O. Stelling, and F. Feigl and M. Fürth; with **phenylbiguanidine**, by A. Smolka and A. Friedreich; with **benzidine**, by G. Spacu; with **diacetonitrile**, by F. Schlegel, and A. Naumann; with **diacetyloximes**, by J. Beato and M. de los D. Brugger, and K. Friedrich; with **camphidine**, by M. R. Menz; with **aldoximene**, by W. Hieber and co-workers; with **ketoxyms**, by W. Hieber and F. Leutert; with **dimethylglyoxime**, **diacetyldioxime**, and **methylthioacetyldioxime**, by F. Feigl and H. Rubinstein, K. Friedrich, F. Paneth and E. Thilo, E. Thilo, and J. V. Dubsky and F. Brychta; with **thiosemicarbazide**, by K. A. Jensen and E. R. Madsen; and J. V. Dubsky and A. Rabas obtained no complex with **glycine**; and G. Fuseya and K. Murata, none with **glycocol**. Compounds with **pyridine** were obtained by W. Biltz and co-workers, W. Hieber and E. Levy, W. R. Brode, A. Classen and B. Zahorsky, A. Hantzsch and co-workers, W. Hieber and A. Woerner, N. S. Kurnakoff, W. Lang, S. von Laszczynsky, A. T. Lincoln, J. N. Pearce, E. G. V. Percival and W. Wardlaw, F. Reitzenstein, I. Rohde and E. Vogt, F. Schlegel, G. Spacu and L. Caton, O. Stelling, R. Weinland and co-workers, and A. Werner and co-workers. J. N. Pearce and T. E. Moore gave for the percentage solubility:

S . . .	-48.2°	-50.3°	-30°	+15°	25°	70°	78.2°	90°	11.0°
	0	—	0.42	—	0.57	—	2.28	—	14.16
Solid phase	Py		CoCl <sub>2</sub> .6Py		CoCl <sub>2</sub> .4Py		CoCl <sub>2</sub> .2Py		CoCl <sub>2</sub>

Complexes with  **$\alpha$ -acetaminopyridine** were observed by F. L. Hahn and co-workers; with **piperidine**, by A. Werner and co-workers; with **dipyridyl**, by F. Blau; with **quinoline**, by E. Beckmann, E. G. V. Percival and W. Wardlaw, F. Borsbach, J. N. Pearce, W. R. Brode, and F. Reitzenstein; with **quinoline**, by E. G. V. Percival and W. Wardlaw; with **puridino-2, 3-thiophene**, by W. Steinkopf and G. Lützkendorf; with **phenanthroline**, by F. Blau; and with **thiocarbamide**, by A. Rosenheim and V. J. Meyer. N. V. Konduiroff and D. A. Fomin studied the action of cobalt chloride, on **organomagnesium compounds**. C. Dufraisse and D. Nakae studied the catalytic action of cobalt chloride on the oxidation of **acraldehyde**, **phenylformaldehyde**, **furfuraldehyde**, **styrene**, and **turpentine**; W. Thomson and F. Lewis, the action on **india-rubber**. E. G. Fuelnegg and G. Konopatsch studied the action of cobalt chloride as siccative or drier in various **oils**. J. E. Heck and M. G. Mellon studied rhythmic precipitations with **silicic acid**.

According to Z. Roussin, D. Vitali, D. Tommasi, A. Commaille, S. Kern, and K. Seubert and A. Schmidt, **magnesium** precipitates hydrated cobaltous oxide, mixed with a basic chloride, from neutral soln. of cobalt chloride, and at the same time some hydrogen is evolved; but feebly acidified soln. may be reduced. E. S. Hedges and J. E. Myers said that a magnesium-cobalt couple is produced when magnesium is dipped in a soln. of cobaltous chloride. According to Z. Roussin, and A. Commaille, neutral soln., hot or cold, give no precipitate with **zinc**, but if a third metal—lead or copper—is present, L. de Boisbaudron observed that the soln. may be reduced; and A. F. Gehlen, and J. L. Davies observed that an ammoniacal soln. may be reduced by zinc—*vide supra*, metallic precipitation of cobalt. M. Dombrow found that hydrated cobaltous chloride when heated with zinc, gives a violent reaction with the liberation of hydrogen. The precipitation of cobalt from soln. of the chloride in absolute alcohol by zinc, and **cadmium**, was studied by R. Müller and F. R. Thoïs. C. Formenti and M. Levi studied the reducing action of **aluminium**. H. Schulze found that, at a red-heat, **tungstic oxide** reacts with cobalt chloride in a current of carbon dioxide:  $2\text{WO}_3 + \text{CoCl}_2 = \text{CoWO}_4 + \text{WO}_2\text{Cl}_2$ . M. Curie and J. Saddy found cobalt chloride reduced the luminescence of **zinc sulphide**. D. Längauer studied the system:  $\text{CoCl}_2 + \text{K}_2\text{SO}_4 \rightleftharpoons 2\text{KCl} + \text{CoSO}_4$ . G. and P. Spacu obtained complex salts with **silver iodide**. E. Montignie observed that with **mercuric oxide**, cobaltous hydroxide, and with a small proportion of mercuric oxide, an oxychloride,  $\text{CoCl}_2.3\text{CoO}.3\text{H}_2\text{O}$ , is formed.

**The double salts of cobaltous chloride.**—The formation of solid soln. from soln. of chlorides and dihydrated cobalt chloride was discussed by A. Johnsen, O. Lehmann, and J. M. Merrick, and it is doubtful if a double salt is formed. The crystals of the solid soln. were examined by A. Neuhaus, J. W. Retgers, P. Gaubert, J. L. C. Schroeder van der Kolk, and B. Srebroff. H. W. Foote found that with soln., at 25°, containing the following percentage proportions of:

NH <sub>4</sub> Cl	17.90	13.59	8.75	7.62	7.45
CoCl <sub>2</sub>	15.63	25.19	34.28	34.61	35.24
Solid phase	Solid soln. NH <sub>4</sub> Cl. <i>n</i> CoCl <sub>2</sub> .2H <sub>2</sub> O			Solid soln. + CoCl <sub>2</sub> .6H <sub>2</sub> O	

There is the possibility that the solid phases contain isomorphous mixtures, or solid soln., of ammonium chloride and some double salt which is unstable when alone, for cases are known where two salts crystallize isomorphously to form a stable hydrate which neither salt yields when alone—*e.g.*, the monoclinic monohydrated copper and zinc sulphates. A. Benrath's results, at 25°, with the mol. proportions of the dissolved salt as abscissæ, and the number of mols. of water per mol. of dissolved salt as ordinates, are plotted in Fig. 90. F. W. J. Clendinnen, and A. C. D. Rivett and F. W. J. Clendinnen studied the ternary system: CoCl<sub>2</sub>—NH<sub>4</sub>Cl—H<sub>2</sub>O, at 60°, in order to avoid complications with hydrates higher than CoCl<sub>2</sub>.2H<sub>2</sub>O. The results are summarized in Fig. 83. There is no indication of the formation of a double salt at this temp. There is a region of metastability bounded by dotted lines. The composition of the solid soln. can be represented by points on the line AD, which is continuous from ammonium chloride to dihydrated cobalt chloride.

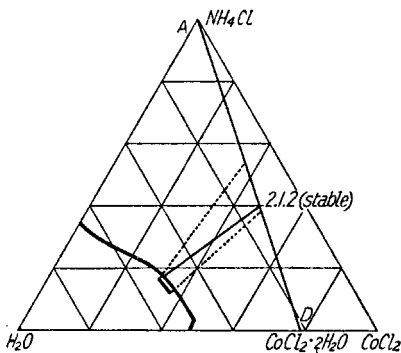


FIG. 83.—The Ternary System :  
NH<sub>4</sub>Cl—CoCl<sub>2</sub>—H<sub>2</sub>O at 60°.

O. Hautz reported hydrated **ammonium cobaltous trichloride**, NH<sub>4</sub>Cl.CoCl<sub>2</sub>.6H<sub>2</sub>O, to be formed from soln. of cobalt and ammonium chlorides in equivalent proportions. G. Rosenheim and M. Platsch also prepared this salt. O. Hautz added that the crystals are always contaminated with those of ammonium chloride, and have to be purified by crystallization. The ruby-red, monoclinic crystals are deliquescent in moist air, and are freely soluble in water. F. Rose heated cobaltous hexamminochloride in air, and obtained what he regarded as **ammonium cobaltous amminotrichloride**, NH<sub>4</sub>Cl.CoCl<sub>2</sub>.NH<sub>3</sub>, but W. Biltz said that the analysis agrees better with NH<sub>4</sub>Cl.CoCl<sub>2</sub>. $\frac{1}{2}$ NH<sub>3</sub>. W. Biltz and B. Fetkenheuer could not prepare a definite compound by the method of F. Rose, but they obtained a product CoCl.(NH<sub>4</sub>Cl)O<sub>2</sub>.NH<sub>3</sub> by heating at 310° to 320° a mixture of cobaltous chloride and ammonium chloride in ammonia.

H. Franzen and H. L. Lucking obtained **hydrazine cobaltous tetrachloride**, CoCl<sub>2</sub>(N<sub>2</sub>H<sub>4</sub>.HCl)<sub>2</sub>.2H<sub>2</sub>O. A. Ferratini prepared a **hydrazine cobaltous hydrazino-chloride**, 2N<sub>2</sub>H<sub>5</sub>Cl.CoCl<sub>2</sub>. $\frac{1}{2}$ N<sub>2</sub>H<sub>4</sub>, from an aq. soln. of the components. The product was boiled in alcohol, and a mixture of wine-red, and violet crystals separated out. The violet crystals are separated mechanically. The salt furnishes prismatic needles which melt at 221° to 223°, and they are soluble in water, and in aq. alcohol.

Cobaltous chloride does not form a **potassium cobaltous chloride**. C. Mazzetti examined the system: KCl—CoCl<sub>2</sub>—H<sub>2</sub>O, at 20°, and observed no signs of a double salt. Expressing the composition of sat. soln. in percentages, he found:

CoCl <sub>2</sub>	33.52	33.15	31.58	28.37	20.25	7.40
KCl	4.73	6.81	6.79	7.70	11.56	19.37
Solid phases	CoCl <sub>2</sub> .6H <sub>2</sub> O + KCl			KCl		



The results are plotted in Fig. 86. A. Benrath's results at 25° are indicated in Fig. 89. H. W. Foote also observed no double salt is formed at 25°. The univariant point in the system is 8.24 per cent. KCl, and 32.91 per cent.  $\text{CoCl}_2$ ; this is very close to the value obtained by C. Mazzetti at 20°. J. Kendall and K. P. Monroe, and N. A. Yajnik and R. L. Uberoy measured the sp. gr. and viscosity of mixed soln. of the two chlorides; and J. Trötsch, and G. Akerlöf and H. C. Thomas, the electrical conductivity. H. W. Foote obtained for the system:  $\text{RbCl}-\text{CoCl}_2-\text{H}_2\text{O}$ , at 25°:

$\text{CoCl}_2$	35.67	35.11	34.58	34.29	31.74	16.09	11.37	5.41	0
$\text{RbCl}$	0	5.98	6.83	7.79	9.34	30.52	38.03	43.58	48.57
Solid phases	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$		$\text{RbCl} \cdot \text{CoCl}_2 \cdot 2\text{H}_2\text{O}$		$2\text{RbCl} \cdot \text{CoCl}_2 \cdot 2\text{H}_2\text{O}$		$\text{RbCl}$		

The results are plotted in Fig. 84. There are formed hydrated **rubidium cobaltous trichloride**,  $\text{RbCl} \cdot (\text{CoCl}_2 \cdot 2\text{H}_2\text{O})$ , and hydrated **rubidium cobaltous tetrachloride**,

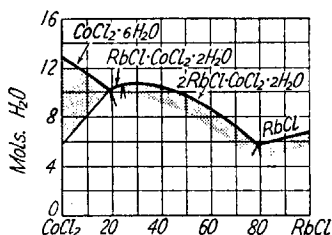


FIG. 84.—The Ternary System :  $\text{RbCl}-\text{CoCl}_2-\text{H}_2\text{O}$ , at 25°.

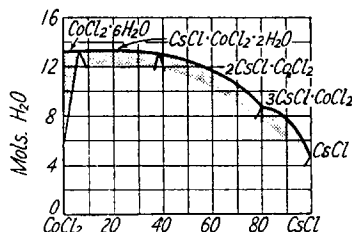


FIG. 85.—The Ternary System :  $\text{CsCl}-\text{CoCl}_2-\text{H}_2\text{O}$ , at 25°.

$2\text{RbCl} \cdot \text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ . The univariant points are 6.09 per cent.  $\text{RbCl}$  and 35.02 per cent.  $\text{CoCl}_2$ ; 7.68 per cent.  $\text{RbCl}$  and 34.36 per cent.  $\text{CoCl}_2$ ; and 38.43 per cent.  $\text{RbCl}$  and 11.51 per cent.  $\text{CoCl}_2$ . A. Benrath could not find the trichloride obtained by H. W. Foote, but obtained the tetrachloride. A. Benrath's results for the system:  $\text{RbCl}-\text{CoCl}_2-\text{H}_2\text{O}$ , at 25°, are plotted in Fig. 87, where, as before, the per-

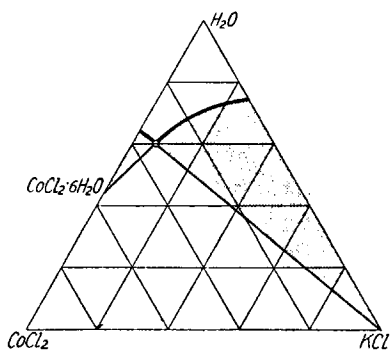


FIG. 86.—The Ternary System :  $\text{KCl}-\text{CoCl}_2-\text{H}_2\text{O}$ , at 20°.

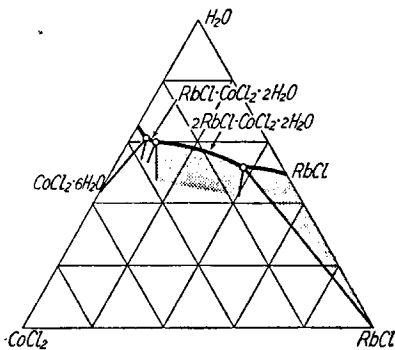


FIG. 87.—The Ternary System :  $\text{RbCl}-\text{CoCl}_2-\text{H}_2\text{O}$ , at 25°.

centage proportions of the two component salts,  $\text{CoCl}_2$ , and  $\text{RbCl}$ , are plotted as abscissæ, and the number of mols. of water per mol. of mixed salt, as ordinates. A. Benrath's results for the ternary system:  $\text{CsCl}-\text{CoCl}_2-\text{H}_2\text{O}$ , at 25°, are plotted similarly in Fig. 85, and they agree with those obtained by H. W. Foote, where the compositions of the sat. soln. are expressed in percentages:

$\text{CoCl}_2$	35.67	35.73	32.58	31.09	22.57	8.98	7.75	0.25	0
$\text{CsCl}$	0	1.65	3.62	5.03	16.22	40.56	42.76	65.48	65.61
Solid phases	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$		$\text{CsCl} \cdot \text{CoCl}_2 \cdot 2\text{H}_2\text{O}$		$2\text{CsCl} \cdot \text{CoCl}_2$		$3\text{CsCl} \cdot \text{CoCl}_2$		$\text{CsCl}$

The hexahydrate of cobalt chloride as solid phase has the invariant point 1.86 per cent. CsCl and 35.67 per cent.  $\text{CoCl}_2$ , where the second phase is hydrated **caesium cobaltous trichloride**,  $\text{CsCl} \cdot \text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ —E. H. Ducloux reported crystals of the anhydrous salt—there is then another invariant point for 5.03 per cent. CsCl and 31.09 per cent.  $\text{CoCl}_2$ , where the other solid phase is **caesium cobaltous tetrachloride**,  $2\text{CsCl}_2 \cdot \text{CoCl}_2$ ; there is then an invariant point at 40.56 per cent. CsCl and 8.98 per cent.  $\text{CoCl}_2$ , with the other solid phase **caesium cobaltous pentachloride**,  $3\text{CsCl} \cdot \text{CoCl}_2$ ; and there is then the invariant point at 65.48 per cent. CsCl and 0.25 per cent.  $\text{CoCl}_2$ , with caesium chloride as the other solid phase. O. Stelling and F. Olsson studied the X-ray absorption spectrum of  $\text{CsCl} \cdot \text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ ; E. H. Ducloux obtained crystals of  $2\text{CsCl} \cdot \text{CoCl}_2$ ; and J. Vermande, crystals of  $3\text{CsCl} \cdot \text{CoCl}_2$ . These three caesium cobaltous salts were prepared by G. F. Campbell from mixed soln. of the component salts. Small plates of the trichloride were deposited from soln. in which the ratio Cs : Co varies from 0.4 : 1 to a syrupy soln. of cobaltous chloride; large plates or prisms of the tetrachloride, from soln. with Cs : Co ranging from 6 : 1 to 0.4 : 1; and combinations of cubic and octahedral crystals of the pentachloride, from soln. with Cs : Co ranging from 12 : 1 to 6 : 1. Each soln. was acidified with hydrochloric acid. G. and P. Spacu observed the formation of the **caesium cobalt amminotetrachlorides**,  $\text{Cs}_2[\text{CoCl}_4] \cdot 9\text{NH}_3$ —the vap. press., at  $-82^\circ$ , are :

Mols. $\text{NH}_3$ . .	12.66	11.00	10.74	9.97	9.74	9.18	8.92	8.86
p mm. . . .	28.5	27.5	26.0	26.00	24.0	15.0	6.0	2.0

$\text{Cs}_2[\text{CoCl}_4] \cdot 5\text{NH}_3$ —with the vap. press. 6, 10.5, and 38.0 mm., respectively, at  $0^\circ$ ,  $16.9^\circ$ , and  $78^\circ$ , and the heat of formation from the double salt, 14.20 Cals. per mol. of  $\text{NH}_3$ ;  $\text{Cs}_2[\text{CoCl}_4] \cdot 2\text{NH}_3$ —with the vap. press. 19 mm. at  $78^\circ$ , and the heat of formation, 16.97 Cals. per mol. of  $\text{NH}_3$ ; and  $\text{Cs}_2[\text{CoCl}_4] \cdot \text{NH}_3$ —with the vap. press. 19, 7, 3, 0.9 mm., respectively, for 1.34, 1.15, 1.12, and 1.09 mols. of  $\text{NH}_3$ .

C. Mazzetti found that soln. of cobaltous and sodium chlorides, treated in a similar manner, at  $20^\circ$ , gave no evidence of the formation of a **sodium cobaltous chloride**. Expressing concentrations in percentages of the anhydrous salts, sat. soln. contain :

$\text{CoCl}_2$ . . . .	34.98	33.38	33.05	32.84	21.45	8.20	0
$\text{NaCl}$ . . . .	0	3.35	3.65	3.91	10.32	19.40	26.09
Solid phases	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$				$\text{NaCl}$		

The results are plotted in Fig. 89. H. W. Foote obtained similar results at  $25^\circ$ ,

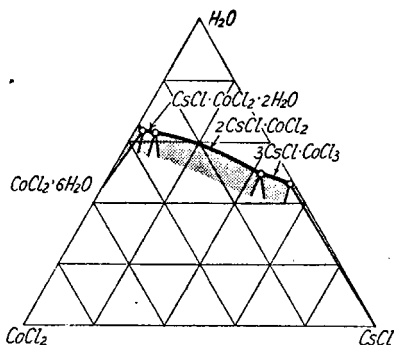


FIG. 88.—The Ternary System :  
 $\text{CsCl} - \text{CoCl}_2 - \text{H}_2\text{O}$ , at  $25^\circ$ .

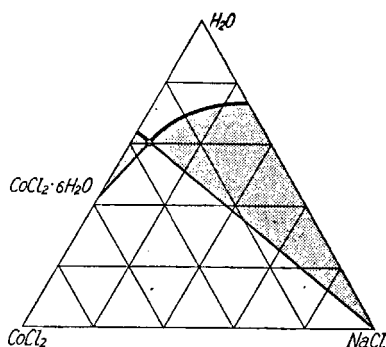


FIG. 89.—The Ternary System :  
 $\text{NaCl} - \text{CoCl}_2 - \text{H}_2\text{O}$ , at  $20^\circ$ .

and he found the invariant point corresponds with 4.70 per cent. of sodium chloride and 32.91 per cent. of cobaltous chloride. A. Benrath found at  $25^\circ$  and  $98^\circ$  the mol.

percentages of NaCl to  $\text{CoCl}_2$  in soln., and the number of mols. of water per mol. of mixed salt :

25°	NaCl	0	9.37	27.90	45.3	69.0	83.0	97.0	100 per cent.
	$\text{H}_2\text{O}$	6.67	6.15	5.49	7.56	8.32	8.48	8.58	8.33 mols.
98°	NaCl	0	15.7	25.2	34.2	57.7	65.4	86.6	100 per cent.
	$\text{H}_2\text{O}$	12.65	10.7	9.95	8.39	8.15	8.28	7.44	7.44 mols.

M. Löffler studied solid soln. with sodium chloride. C. Mazzetti, J. Kendall and K. P. Monroe, and N. A. Yajnik and R. L. Uberoy measured the viscosity of

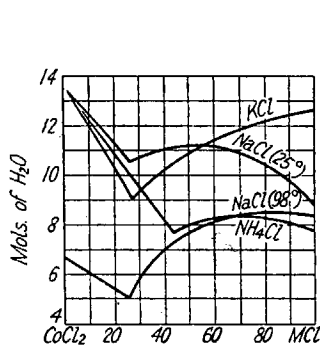


FIG. 90.—The Ternary System :  
 $\text{MCl}-\text{CoCl}_2-\text{H}_2\text{O}$ , at 25°.

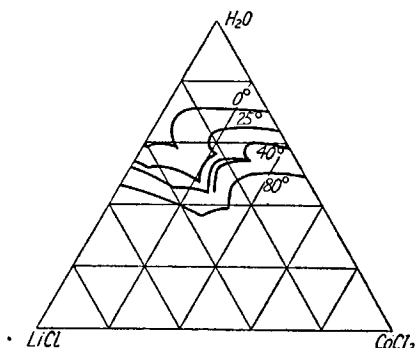


FIG. 91.—The Ternary System :  
 $\text{LiCl}-\text{CoCl}_2-\text{H}_2\text{O}$ .

mixed soln. of the two salts ; A. Benrath, the raising of the b.p. ; and C. Mazzetti, and J. Trötsch, the electrical conductivity. A. Chassevant reported hydrated **lithium cobaltous trichloride**,  $\text{LiCl} \cdot \text{CoCl}_2 \cdot 3\text{H}_2\text{O}$ , to be formed from soln. of the component salts, and he obtained the anhydrous salt by dehydration in a desiccator. The acicular crystals effloresce in a dry atmosphere and lose hydrogen chloride ; they are dissociated by water, but are stable in the presence of an excess of lithium chloride. The crystals are isomorphous with the corresponding salts of manganese, iron, and nickel. J. Kendall and K. P. Monroe, and N. A. Yajnik and R. L. Uberoy studied the sp. gr. and viscosity of the mixed soln. of the component salts ; and R. Engel, their colour. H. Bassett and H. H. Croucher formulate the compound :  $[\text{Li}(\text{H}_2\text{O})_2][\text{Co}(\text{H}_2\text{O})\text{Cl}_3]$  ; A. Benrath examined the ternary system :  $\text{LiCl}-\text{CoCl}_2-\text{H}_2\text{O}$ , at 25°, and found for the percentage mol. proportions of lithium

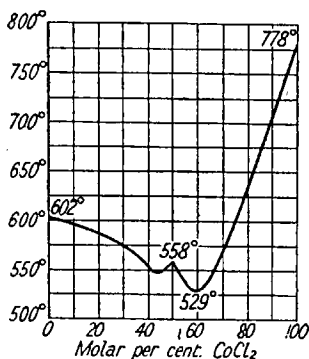


FIG. 92.—Melting-point Curve of Lithium  
and Cobaltous Chlorides.

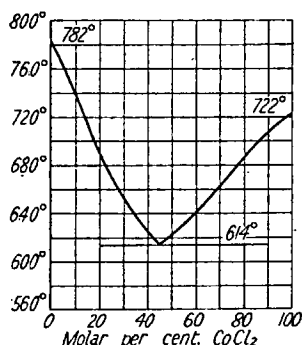


FIG. 93.—Melting-point Curve of Calcium  
and Cobaltous Chlorides.

chloride to cobalt chloride—abscissæ in Fig. 91—and the corresponding proportions of water mols. per mol. of mixture—ordinates in Fig. 85 :

LiCl <sub>2</sub>	0	32.1	64.57	64.80	75.40	77.8	93.68	96.25	100 per cent.
H <sub>2</sub> O	12.6	12.2	6.96	7.14	5.31	5.46	5.48	5.51	5.71 mols.
Solid phases		CoCl <sub>2</sub> .6H <sub>2</sub> O	CoCl <sub>2</sub> .2H <sub>2</sub> O	4LiCl.CoCl <sub>2</sub> .10H <sub>2</sub> O				LiCl.H <sub>2</sub> O	

The results indicate the formation of hydrated **lithium cobaltous hexachloride**, 4LiCl.CoCl<sub>2</sub>.10H<sub>2</sub>O. H. Bassett and H. H. Croucher doubt the existence of this salt. J. W. Retgers observed that in the presence of conc. hydrochloric acid, lithium chloride separates from the mixed soln. A. Ferrari and A. Baroni showed that the m.p. curve of mixtures of cobalt and lithium chlorides, Fig. 92, has a maximum corresponding with the formation of **lithium cobaltous tetrachloride**, Li<sub>2</sub>CoCl<sub>4</sub>, m.p. 558°. H. Bassett and I. Sanderson examined the ternary system: LiCl-CoCl<sub>2</sub>-H<sub>2</sub>O at 0°, 25°, 40°, and 80°, and the results are summarized in Fig. 91. They observed **lithium cobaltous hexachloride**, 7LiCl.2CoCl<sub>2</sub>.18H<sub>2</sub>O; **lithium cobaltous heptachloride**, 3LiCl.2CoCl<sub>2</sub>.6H<sub>2</sub>O; and the dihydrate of the trichloride as well as of solid soln. between lithium cobaltous tetrachloride, 2LiCl.CoCl<sub>2</sub>.2H<sub>2</sub>O, and LiCl.H<sub>2</sub>O.

A. Mailhe boiled a soln. of cobalt chloride with hydrated cupric oxide and obtained grey crystals of a **copper cobaltous trioxodichloride**, CoCl<sub>2</sub>.3CuO.4H<sub>2</sub>O.

A. Werner represented the salt by the formula:

Cu<sub>2</sub>(OH)<sub>4</sub>.Cu(OH)<sub>2</sub>.CoCl<sub>2</sub>.H<sub>2</sub>O. The green crystals

are isomorphous with those of the corresponding

nickel salt. W. A. Endriss made observations on

this subject. R. Engel thought that a **calcium**

**cobaltous chloride** was formed in a mixed soln. of

the component chlorides. A. Ferrari and A. Inganni

showed that the m.p. curve, Fig. 93, is of the simple

V-type, with a eutectic at 614°, and 54.3 per cent. of

CaCl<sub>2</sub>. A. Benrath examined the ternary system:

CaCl<sub>2</sub>-CoCl<sub>2</sub>-H<sub>2</sub>O, at 25°, and found for the per-

centage mol. proportions of calcium chloride to

cobalt chloride—abscissæ, Fig. 96—and the corre-

sponding proportions of water mols. per mol. of

mixture—ordinates in Fig. 96:

CaCl <sub>2</sub>	0	30.78	45.6	67.7	78.2	84.9	94.8	100 per cent.
H <sub>2</sub> O	12.63	11.48	10.94	9.62	8.58	6.54	7.18	7.21 mols.
Solid phases			CoCl <sub>2</sub> .6H <sub>2</sub> O				CaCl <sub>2</sub> .6H <sub>2</sub> O	

There is no sign of the formation of a double salt. H. C. Jones and W. W. Strong,

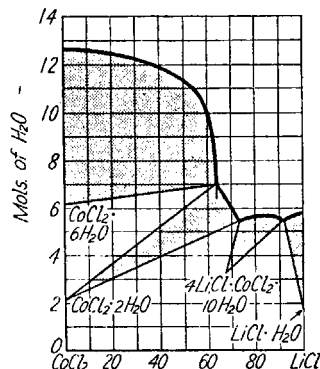


FIG. 95.—The Ternary System:  
LiCl-CoCl<sub>2</sub>-H<sub>2</sub>O, at 25°.

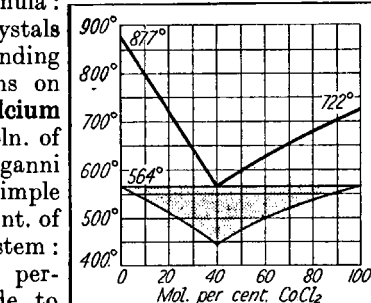


FIG. 94.—Freezing-point  
Curves of the System:  
SrCl<sub>2</sub>-CoCl<sub>2</sub>.

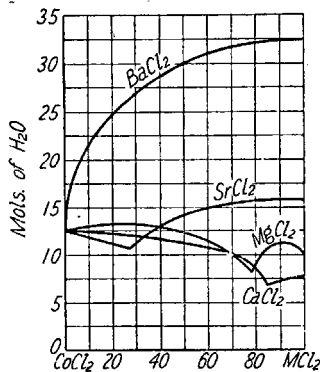


FIG. 96.—The Ternary System:  
MCl<sub>2</sub>-CoCl<sub>2</sub>-H<sub>2</sub>O, at 25°.

and W. J. Russell studied the absorption spectrum of mixed soln. of the two salts; H. C. Jones and H. S. Uhler, the f.p. of the soln.; A. Benrath, the b.p.;

H. C. Jones and H. S. Uhler, the electrical conductivity; and F. G. Donnan and H. Bassett, the transport numbers, and constitution of the aq. soln. Similarly, A. Benrath obtained no sign of the formation of a **strontium cobaltous chloride** in his study of the ternary system:  $\text{SrCl}_2\text{-CoCl}_2\text{-H}_2\text{O}$ , at  $25^\circ$ , Fig. 96, when he found:

$\text{SrCl}_2$	.	.	.	0	17.92	27.15	41.01	78.5	100 per cent.
$\text{H}_2\text{O}$	.	.	.	12.65	11.40	10.68	13.01	15.05	15.85 mols.
Solid phases				$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$			$\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$		

A. Benrath obtained the curve, Fig. 96, for C. Mazzetti's data, for the system:  $\text{BaCl}_2\text{-CoCl}_2\text{-H}_2\text{O}$ , at  $25^\circ$ . A. Ferrari and A. Inganni observed no sign of a strontium cobaltous chloride on the f.p. curves of the system:  $\text{SrCl}_2\text{-CoCl}_2$ , Fig. 94. There is no miscibility in the solid state, and there is a eutectic at  $564^\circ$ , and 40.5 mols. per cent. of cobaltous chloride. C. Mazzetti examined the ternary system:  $\text{BaCl}_2\text{-CoCl}_2\text{-H}_2\text{O}$ , at  $20^\circ$ , and observed no sign of the formation of a **barium cobaltous chloride**. The percentage composition of the sat. soln. are:

$\text{CoCl}_2$	.	34.43	34.15	33.80	29.57	24.92	19.52	13.14	6.34
$\text{BaCl}_2$	.	0.45	0.37	0.38	0.88	2.01	5.48	10.03	16.50

The results of his study of the viscosity and electrical conductivity of mixed soln. of cobalt and barium chlorides were interpreted on the assumption that complex ions were formed.

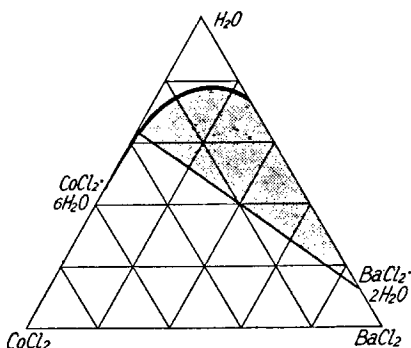


FIG. 97.—The Ternary System :  $\text{BaCl}_2\text{-CoCl}_2\text{-H}_2\text{O}$ , at  $20^\circ$ .

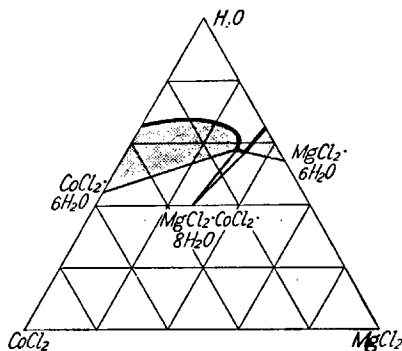


FIG. 98.—The Ternary System :  $\text{MgCl}_2\text{-CoCl}_2\text{-H}_2\text{O}$ , at  $20^\circ$ .

H. Bassett and H. H. Croucher examined the ternary system:  $\text{MgCl}_2\text{-CoCl}_2\text{-H}_2\text{O}$ , at  $25^\circ$ . Expressing concentrations in percentages, they found for sat. soln.:

$\text{CoCl}_2$	.	35.87	28.78	12.08	12.43	10.00	8.95	8.44	4.44	0.00
$\text{MgCl}_2$	.	0.00	6.20	29.04	28.89	31.00	31.66	31.95	34.00	36.20
Solid phases		$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$			$\text{MgCl}_2 \cdot \text{CoCl}_2 \cdot 8\text{H}_2\text{O}$			$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$		

The results are plotted in Fig. 98. There is clear evidence of the formation of a blue, hydrated **magnesium cobaltous tetrachloride**,  $\text{MgCl}_2 \cdot \text{CoCl}_2 \cdot 8\text{H}_2\text{O}$ . There was no evidence of the isomorphism of the hexahydrated magnesium and cobaltous chlorides. It is assumed, on the basis of the work of F. G. Donnan and H. Bassett, cited above, that the blue salt contains a complex cobalt anion, and they favour the hypothesis that the salt is constituted:  $[\text{Mg}(\text{H}_2\text{O})_4]^{+}[\text{CoCl}_4]^{-}$ . The salt appears in deep blue rhombohedra, but small crystals have a reddish tinge in transmitted light. The results agree with observations by E. G. V. Percival and W. Wardlaw on complex salts of pyridine, quinoline, and quinaldine with the anion  $\text{CoCl}_4^{--}$ . A. Benrath's results for the system:  $\text{MgCl}_2\text{-CoCl}_2\text{-H}_2\text{O}$ , at  $25^\circ$ , are summarized in Fig. 96, the compound salt was not recognized. A. Ferrari and A. Inganni studied

the m.p. curve, and the results, summarized in Fig. 99, show no signs of a double salt at these temp. There is a continuous series of solid soln. J. Kendall and K. P. Monroe, A. Benrath, and N. A. Yajnik and R. L. Uberoy measured the sp. gr. and viscosity of the mixed soln.

A. Ferrari and A. Inganni obtained the curve, Fig. 101, for zinc and cobaltous chlorides. There is no sign of a zinc cobaltous chloride, there is no miscibility, and the eutectic temp. is the same as the m.p. of zinc chloride, namely  $300^{\circ}$ . H. Bassett and W. L. Bedwell also measured the f.p. of the mixtures, and found that the two curves descended from  $735^{\circ}$ , the f.p. of cobalt chloride, and  $313^{\circ}$ , the m.p. of zinc chloride, and met at the eutectic, which is between  $311^{\circ}$  and  $313^{\circ}$ , very near the m.p. of zinc chloride alone. The one curve corresponds with the separation of cobalt chloride in freezing, and the other curve corresponds with the separation of solid soln. of up to 7 per cent. of cobalt chloride in zinc chloride. The colour of the mixtures is like that of anhydrous cobalt chloride. They emphasized the fact that whilst the hydrated chlorides form definite compounds, the anhydrous chlorides do not do so; and this shows that it is unsafe to assume that a hydrated double or complex salt will remain a chemical individual after dehydration.

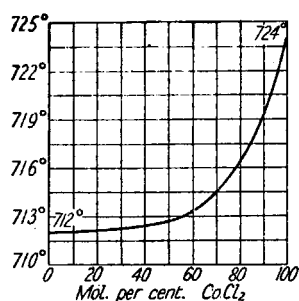


Fig. 99.—The Fusion Curve of the System:  $\text{MgCl}_2\text{-CoCl}_2$ .

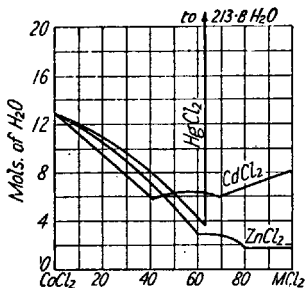


Fig. 100.—Ternary Systems:  $\text{MCl}_2\text{-CoCl}_2\text{-H}_2\text{O}$ , at  $25^{\circ}$ .

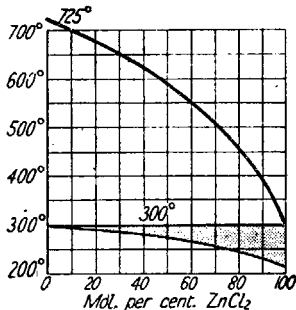


Fig. 101.—Freezing-point Curves of the System:  $\text{ZnCl}_2\text{-CoCl}_2$ .

A. Benrath's observations on the ternary system:  $\text{ZnCl}_2\text{-CoCl}_2\text{-H}_2\text{O}$ , at  $25^{\circ}$ , are summarized in Fig. 100. The first portion of the curve has the hexahydrate,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , as solid phase, and the last portion has hydrated zinc chloride as solid phase. In between there is a curve supposed to represent the compound hydrated zinc cobalt hexachloride,  $2\text{ZnCl}_2 \cdot \text{CoCl}_2 \cdot 12\text{H}_2\text{O}$ , analogous to  $\text{CdCl}_2 \cdot \text{CoCl}_2 \cdot 12\text{H}_2\text{O}$ , obtained in the soln. with cadmium and cobalt chlorides. This was not confirmed by H. Bassett and H. H. Croucher. These investigators found that the equilibrium conditions are not so simple as those indicated in Fig. 100, because of the complications introduced by the hydrolysis of the zinc chloride and by the formation of solid soln. The following is a selection from an extensive series of readings, where the concentrations of sat. soln. are expressed in percentages, and the Greek letters refer to solid soln.:

$\text{CoCl}_2$	35.87	31.20	29.48	13.51	12.61	17.23	4.19	0.61	—	2.60
$\text{ZnCl}_2$	0	27.91	33.31	60.09	63.40	57.95	77.38	80.02	81.28	78.58
	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$		$\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$	$\alpha$	$\beta$	$\gamma$	$\delta$	$\epsilon$	$\text{ZnCl}_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$	

The results are summarized in Fig. 102. The isotherm of the system consists of eight well-marked portions. The soln. richest in cobalt chloride are in equilibrium with the hexahydrate. Addition of zinc chloride causes, first, a fall in the amount of cobalt chloride present in the soln. (reckoned as a percentage of the total weight of soln.), followed by a slight rise until, when the soln. contains 31.20 per cent. of cobalt chloride and 27.91 per cent. of zinc chloride, the dihydrate,  $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ , becomes the stable solid phase. Its range of existence is comparatively short,

and at 29.48 per cent.  $\text{CoCl}_2$  and 33.31 per cent.  $\text{ZnCl}_2$ , hydrated **zinc cobaltous tetrachloride**,  $\text{CoCl}_2 \cdot \text{ZnCl}_2 \cdot 6\text{H}_2\text{O}$ , appears. From this point to 13.60 per cent.  $\text{CoCl}_2$  and 60.09 per cent.  $\text{ZnCl}_2$ , there is a solid phase consisting of a series of solid soln.— *$\alpha$ -solid solutions*—of  $\text{ZnCl}_2 \cdot 3\text{H}_2\text{O}$  in  $\text{ZnCl}_2 \cdot \text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , that is, between  $[\text{Zn}(\text{OH})_6]^{+}[\text{ZnCl}_4]^{-}$  and  $[\text{Co}(\text{H}_2\text{O})_6]^{+}[\text{ZnCl}_4]^{-}$ . These soln. crystallize

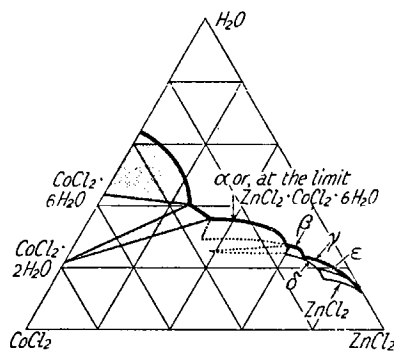


FIG. 102.—The Ternary System :  $\text{ZnCl}_2$ - $\text{CoCl}_2$ - $\text{H}_2\text{O}$ , at  $25^\circ$ .

$[\text{Zn}_2\text{Cl}_6]_2$ . The  $\gamma$ -solid soln. crystallize in long prisms with oblique ends. The  $\gamma$ -solid soln. is in turn replaced by a fourth series— *$\epsilon$ -solid solutions*—as the concentration attains 0.61 per cent.  $\text{CoCl}_2$  and 80.02 per cent.  $\text{ZnCl}_2$ . The constituent of the  $\epsilon$ -solid soln. is  $\text{ZnCl}_2 \cdot 1\frac{1}{3}\text{H}_2\text{O}$ , that is,  $[\text{Zn}(\text{H}_2\text{O})_4]^{+}[\text{Zn}_2\text{Cl}_6]^{-}$ , and the other constituent is  $[\text{Co}(\text{H}_2\text{O})_4]^{+}[\text{Zn}_2\text{Cl}_6]^{-}$ . The  $\epsilon$ -solid soln. furnish clear, 6-sided plates associated, maybe, with pseudomorphs of the  $\delta$ -solid soln. The solubility curves of the  $\gamma$ - and  $\epsilon$ -solid soln. can be followed some distance into the metastable region. There is yet a fifth series of solid soln.— *$\delta$ -solid solutions*—in which  $\text{ZnCl}_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ ,  $[\text{Zn}_2(\text{H}_2\text{O})_6]^{+}[\text{ZnCl}_4]_2^{-}$  is one constituent, and the other constituent is  $[\text{Co}(\text{H}_2\text{O})_6]^{+}[\text{ZnCl}_4]_2^{-}$ . The series of  $\delta$ -solid soln. is metastable over its whole, moderately extensive range; and it furnishes small, diamond-shaped plates, and rhombs rather like those of calcite. Lastly, anhydrous zinc chloride may be obtained at  $25^\circ$  in metastable equilibrium with a limited range of soln. of zinc and cobalt chlorides. F. G. Donnan and H. Bassett studied the colour and constitution of the aq. soln.

C. van Hauer reported **cadmium cobaltous hexachloride**,  $2\text{CdCl}_2 \cdot \text{CoCl}_2 \cdot 12\text{H}_2\text{O}$ , or, according to G. Spacu and L. Caton,  $[\text{CdCl}_6][\text{Cd}(\text{H}_2\text{O})_6][\text{Co}(\text{H}_2\text{O})_6]$ , to be deposited from a soln. of 3 mols. of the cobalt salt to 4 mols. of the cadmium salt allowed to evaporate spontaneously in not too warm a place. A. Benrath studied the ternary system:  $\text{CdCl}_2$ - $\text{CoCl}_2$ - $\text{H}_2\text{O}$ , at  $25^\circ$ , and obtained a curve with the hydrated component salts as solid phases at each end, and this double salt in between, Fig. 99, where the mol. proportions of the two salts are expressed in percentages, are the abscissæ, and the number of mols. of water per mol. of the mixed salt are the ordinates. The data were:

$\text{CdCl}_2$	0	5.14	21.85	40.3	41.1	43.7	57.8	70.4	80.3	100
$\text{H}_2\text{O}$	12.66	11.92	9.37	6.38	6.25	6.44	6.86	6.37	6.93	7.94
		$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$			$2\text{CdCl}_2 \cdot \text{CoCl}_2 \cdot 10\text{H}_2\text{O}$			$(\text{CdCl}_2 \cdot 2\frac{1}{2}\text{H}_2\text{O})$		

The crystals of the complex salt are columnar, and the same in colour as those of hydrated cobalt chloride, and they resemble those of the magnesium and manganese complex salts. J. Grailich said that the rhombic crystals have the axial ratios  $a : b : c = 1.0958 : 1 : 0.3847$ , and that the (100)-cleavage is imperfect. The crystals were also examined by J. Grailich and V. von Lang. A. Ferrari and A. Inganni found the f.p. curves, Fig. 103, show a continuous series of solid soln. H. Bassett

and I. Sanderson also noted the formation of solid soln. C. von Hauer observed that the crystals deliquesce in moist air, but are stable in dry air; they effloresce over sulphuric acid or calcium chloride. They can be dried, without decomposition, in vacuo; they lose 10 mols. of water at 100°; and at a higher temp., the salt melts in its water of crystallization, it then becomes dark blue, and solid. The solid melts at a red-heat and sublimes with partial decomposition. G. Spacu and L. Caton prepared a complex salt with pyridine, namely, **cadmium cobaltous octopyridinohexachloride**,  $2\text{CdCl}_2 \cdot \text{CoCl}_2 \cdot 8\text{C}_5\text{H}_5\text{N}$ .

P. A. von Bonsdorff reported **mercuric cobaltous tetrachloride**,  $\text{HgCl}_2 \cdot \text{CoCl}_2 \cdot 4\text{H}_2\text{O}$ , or, according to H. Bassett and H. H. Croucher,  $[\text{Co}(\text{H}_2\text{O})_4]\text{HgCl}_4$ , to be formed by evaporating a mixed soln. of the component salts. The carmine-red, columnar crystals are isomorphous with the magnesium and iron mercuric salts. R. Varet gave 1.08 Cals. for the heat evolved in mixing soln. of  $\text{CoCl}_2$  and  $2\text{HgCl}_2$ , at 17°, and 0.90 Cal. for soln. of  $\text{CoCl}_2$  and  $\text{HgCl}_2$ , at 18°. A. Hantzsch observed that an alcoholic soln. of cobalt chloride becomes red when treated with mercuric chloride, owing to the formation of a complex salt. A. Benrath studied the ternary system:  $\text{HgCl}_2$ - $\text{CoCl}_2$ - $\text{H}_2\text{O}$ , at 25°, but did not find this complex salt; his data are summarized in Fig. 100. Expressing the concentrations of sat. soln. at 25°, percentages, H. Bassett and H. H. Croucher found:

$\text{CoCl}_2$	35.87	30.69	21.54	20.96	18.02	15.14	4.33	0
$\text{HgCl}_2$	0	15.14	51.00	51.76	57.81	56.54	21.56	6.90
	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$			$\text{HgCl}_2 \cdot \text{CoCl}_2 \cdot 4\text{H}_2\text{O}$		$\text{HgCl}_2$		

The results are plotted in Fig. 104. H. Bassett and H. H. Croucher added that the effect of cobalt chloride in increasing the solubility of mercuric chloride is remarkable and strikingly shows the great tendency of the latter compound to form negative complex ions. The solubility curve of the mercuric chloride is concave to the water-apex of the triangle. This is unusual, for in 3-component systems containing water and two electrolytes, the solubility curves are nearly always convex to this point. This convexity is due to the opposition of two effects, one causing a diminution of solubility, and the other an increase. In the present instance, since mercuric chloride is very slightly ionized, the depressing effect of the chlorine ions from the cobalt chloride is very slight, but their effect in producing  $\text{HgCl}_4^{--}$  complexes is very great. From the first additions of cobalt chloride there is, therefore, an increase in solubility of the mercuric chloride, but the proportionate effect diminishes with increasing additions, and so a concave curve results. F. G. Donnan and H. Bassett, A. Hantzsch and co-workers, and Y. Shibata and co-workers studied the constitution of the soln.

A. Mailhe reported two basic salts obtained by allowing mercuric oxide to stand in contact with soln. of cobalt chloride—**mercuric trioxodichloride**,  $3\text{CoO} \cdot \text{HgCl}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ , as a green powder consisting of 4-sided plates; and **mercuric**

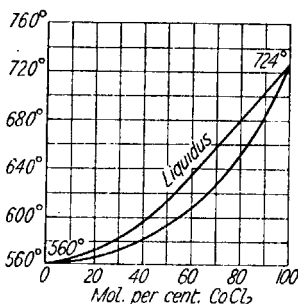


FIG. 103.—The Freezing-point Curves of the System:  $\text{CdCl}_2$ - $\text{CoCl}_2$ .

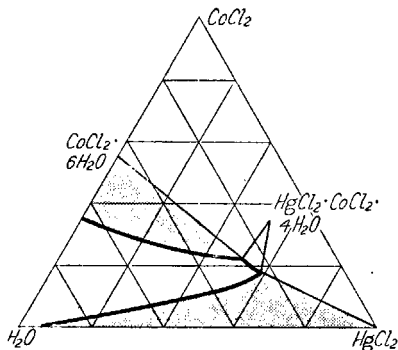


FIG. 104.—The Ternary System:  $\text{HgCl}_2$ - $\text{CoCl}_2$ - $\text{H}_2\text{O}$ .



**hexoxytetrachloride**,  $6\text{CoO} \cdot \text{CoCl}_2 \cdot \text{HgCl}_2 \cdot 20\text{H}_2\text{O}$ , in crystalline granules. G. Spacu and L. Caton reported a complex salt with aniline; F. Calzolari and U. Tagliavini, one with hexamethylenetetramine; and G. Spacu, one with benzidine.

J. Gewecke prepared hydrated **thallic cobaltous octochloride**,  $2\text{TiCl}_3 \cdot \text{CoCl}_2 \cdot 8\text{H}_2\text{O}$ , in hygroscopic, red crystals, by allowing a soln. of the component salts in water, acidified with hydrochloric acid, to evaporate in vacuo over sulphuric acid. S. M. Jørgensen obtained hydrated **cobaltous stannic hexachloride**,  $\text{CoSnCl}_6 \cdot 6\text{H}_2\text{O}$ , by slowly cooling a hot, aq. soln. of equimolar parts of the component salts. J. G. F. Druce oxidized with chlorine a soln. of 7.1 grms. hexahydrated cobalt chloride, and 6.7 grms. of stannous chloride in dil. hydrochloric acid, and then concentrated and cooled the soln. for rose-red crystals. According to S. M. Jørgensen, the rhombohedral crystals have the axial ratio  $a : c = 1 : 0.5103$ , and  $\alpha = 112^\circ 20'$ ; the (101)-cleavage is perfect—*vide* the nickel salt. The crystals deliquesce in moist air; and effloresce in dry air; at  $100^\circ$ , they lose water and stannic chloride. The crystals were examined by H. Töpsøe and C. Christiansen; their sp. gr. is 2.684; S. M. Jørgensen gave 2.298. E. von Biron studied the effect of cobalt chloride on the hydrolysis of stannic chloride in aq. soln. A. Benrath studied the raising of the b.p. of aq. soln. A. Ferrari and C. Colla studied the f.p. of the system:  $\text{SnCl}_2$ - $\text{CoCl}_2$ , Fig. 105, and of the system with lead-cobalt chloride, Fig. 106. In the

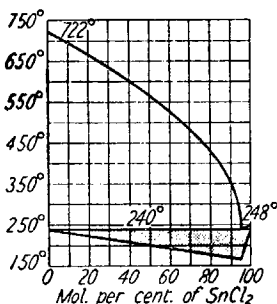


FIG. 105.—The System :  $\text{SnCl}_2$ - $\text{CoCl}_2$ .

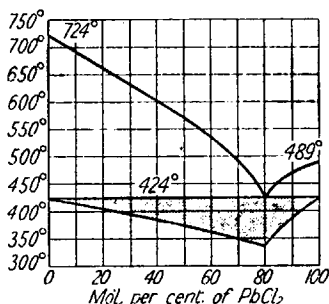


FIG. 106.—The System :  $\text{PbCl}_2$ - $\text{CoCl}_2$ .

former case, there is a eutectic at about  $240^\circ$ , with about 4 mols. per cent. of  $\text{CoCl}_2$ , and in the latter case, at  $424^\circ$ , and 23.5 mols. per cent. of  $\text{CoCl}_2$ .

A. Ferrari and A. Inganni found that the f.p. curve of mixtures of manganese and cobalt chlorides gave no evidence of the formation of a **manganese cobaltous chloride**. There is formed a continuous series of solid soln., Fig. 107. W. Storten-

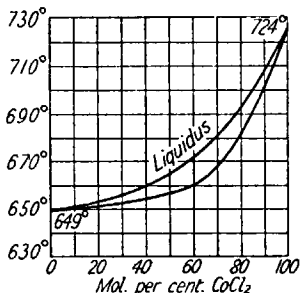


FIG. 107.—Freezing-point Curves of the System :  $\text{CoCl}_2$ - $\text{MnCl}_2$ .

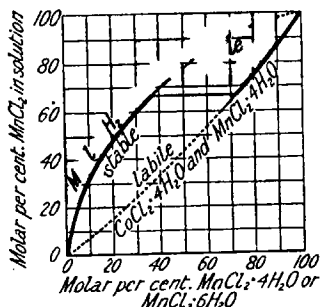


FIG. 108.—Solid Solutions of Manganese and Cobaltous Chlorides.

beker observed that aq. soln. of the two chlorides, containing a mol. of cobalt chloride and 0 to 5 mols. of manganese chlorides, furnish red crystals of the solid

soln. isomorphous with hexahydrated cobaltous chloride. If the soln. contains more than 2 mols. of the manganese chloride, the violet crystals of the solid soln. form spontaneously, and are isomorphous with tetrahydrated manganese chloride. The results with soln. of various concentrations are summarized in Fig. 108.

A. Ferrari and co-workers obtained the f.p. curves of ferrous and cobaltous chlorides, and found no evidence of a **ferrous cobaltous chloride**. A continuous series of solid soln. is formed, Fig. 109. This also agrees with the data from the

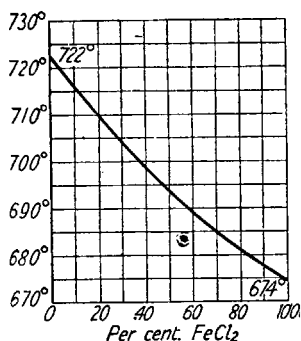


FIG. 109.—Freezing-point Curves of the System:  $\text{FeCl}_2\text{--CoCl}_2$ .

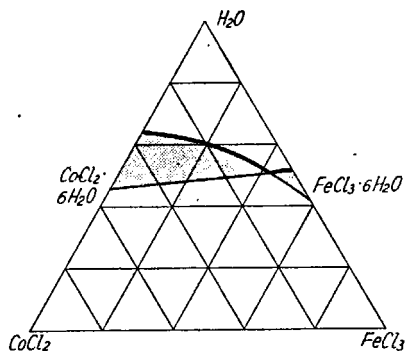


FIG. 110.—The Ternary System:  $\text{FeCl}_3\text{--CoCl}_2\text{--H}_2\text{O}$ , at  $25^\circ$ .

X-radiograms where the lattice parameter  $a$  is 7.05 Å. for cobaltous chloride; 7.075 Å. for  $8\text{CoCl}_2$  and  $2\text{FeCl}_2$ ; 7.095 Å. for  $6\text{CoCl}_2$  and  $4\text{FeCl}_2$ ; 7.115 Å. for  $4\text{CoCl}_2$  and  $6\text{FeCl}_2$ ; 7.135 Å. for  $2\text{CoCl}_2$  and  $8\text{FeCl}_2$ ; and 7.155 Å. for  $\text{FeCl}_2$ . Y. Osaka and T. Yaginuma studied the system:  $\text{FeCl}_3\text{--CoCl}_2\text{--H}_2\text{O}$ , at  $25^\circ$ , and observed no evidence of the formation of a **ferric cobaltous chloride**. Expressing the composition of the sat. soln. in percentages, they found the results indicated in Fig. 110, and:

$\text{FeCl}_3$	.	.	.	0	7.7	41.07	43.28	43.95	47.17	49.42
$\text{CoCl}_2$	.	.	.	30	29.36	7.99	7.40	6.58	2.47	0
Solid phases				$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$				$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$		

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## § 16. Cobaltic Chloride and its Complex Salts

In 1835, G. C. Winkelblech<sup>1</sup> observed that cobaltous chloride cannot be converted into **cobaltic chloride**,  $\text{CoCl}_3$ , by treating it with an excess of chlorine, but when freshly-prepared cobaltic hydroxide is treated with cold hydrochloric acid, the soln. contains some cobaltic chloride. The salt has not yet been isolated. W. Glud and co-workers discussed the preparation of oxygen by a process based on this reaction. In confirmation of the earlier observation, R. J. Meyer and H. Best showed that if alcoholic hydrogen chloride is employed in place of hydrochloric acid, a dark green soln. is produced which soon turns rose-red—presumably the dark green soln. contains cobaltic chloride which soon changes to rose-colour of ordinary cobaltous chloride. C. Schall and H. Markgraf passed chlorine into a soln. of cobaltous chloride in alcohol, or conc. hydrochloric acid at  $-60^\circ$ ; and possibly a tetrachloride is formed at  $-75^\circ$ . C. Schall obtained evidence of the formation of cobaltic chloride in the anodic oxidation of a  $\text{HCl}$ -alcoholic soln. of cobaltous chloride.

### *The $\text{CoA}_6$ or Hexammine Family.*

In 1851, F. A. Genth first prepared *cobaltic luteochloride*, or **cobaltic hexammino-chloride**,  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ , by oxidizing an ammoniacal soln. of a cobaltous salt by exposure to air, and it was afterwards prepared by E. Frémy, O. W. Gibbs and F. A. Genth, and C. D. Braun. E. J. Mills oxidized the soln. with potassium permanganate; A. Carnot, with hydrogen dioxide; G. T. Morgan and J. D. M. Smith, with hydrogen dioxide in an autoclave; C. D. Braun, with lead dioxide; L. Jacobsen, with chlorine; sodium hypochlorite, or bleaching powder; H. and W. Biltz, with iodine; and S. M. Jørgensen, with a nitrate and hydrochloric acid. H. and W. Biltz treated a conc. soln. of cobalt chloride (100 grms.) and ammonium chloride (30 grms.) with a soln. of silver chloride in 20 per cent. aq. ammonia for 24 hrs. at  $40^\circ$ , or 2 days at ordinary temp. The precipitate was extracted with water at  $25^\circ$ ; and the filtrate and washings at  $80^\circ$  were treated with conc. hydrochloric acid to precipitate the silver, and cooled. The product can be re-crystallized from water. The hexammine was also prepared by S. M. Jørgensen, H. and W. Biltz, W. D. Harkins and co-workers, G. T. Morgan and J. D. M. Smith, A. B. Lamb and A. T. Larson, A. Dubosc, and A. Werner and H. Müller, by treating pentammino-salts with hydrochloric acid, or chlorine. P. Pfeiffer discussed the structure of the compounds.

The hexammine occurs in wine-red, or brownish orange-red, dichroic crystals, which J. D. Dana considered to be rhombic, but which were shown by C. Klein, and F. M. Jäger to belong to the monoclinic system, and to have the axial ratios  $a:b:c=0.9880:1:0.6501$ , and  $\beta=91^\circ 19''$ . The needle-like crystals may have rhombic symmetry; no cleavage has been noticed. C. Klein observed twinning about the (001)-plane. H. Lessheim and co-workers, and G. Böttker-Naess and O. Hassel studied the lattice structure. F. M. Jäger gave for the topic axial ratios,  $\chi:\psi:\omega=6.179:6.254:4.006$ ; and 1.704 for the sp. gr. at  $15^\circ$ ; J. D. Dana gave 1.7016 for the sp. gr. at  $20^\circ$ ; W. Biltz and E. Birk, sp. gr. 1.710 at  $25^\circ/4^\circ$ , and mol. vol. 156.4; F. Ephraim and O. Schütz, sp. gr. 1.707 at  $25^\circ/4^\circ$ , and mol. vol. 156.7; G. L. Clark and co-workers, sp. gr. 1.744 at  $25^\circ$ , and mol. vol. 153.37;



and R. Lorenz and I. Posen, and I. Posen, sp. gr. 1.7098 (reduced to a vacuum), and mol. vol., computed for absolute zero, 152.0. W. Biltz and co-workers estimate that the mol. vol. of the ammonia is smaller in cobaltic salts than it is in the cobaltous salts; the mol. vol. of the ammonia in the hexamminochloride is 17; and, according to G. L. Clark and co-workers, 16.09 in comparison with 20 for the cobaltous hexamminochloride. The subject was discussed by R. Klement, E. Birk, and W. Biltz. G. Beck gave 323 Cals. for the heat of formation.

H. Skraup and co-workers, and M. Kidokoro measured the capillary properties of aq. soln. J. Peterson, W. D. Harkins and co-workers, and A. Werner and

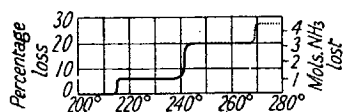


Fig. 111.—The Thermal Dissociation of Cobaltic Hexamminochloride.

C. Herty studied the lowering of the freezing-point of aq. soln., and the results agree with the assumption that the salt is tetra-ionic. E. N. Gapon studied the diffusion of the salt in soln. According to W. Biltz, and G. L. Clark and co-workers, when the dry salt is heated to 215°, it passes into chloropentamminochloride, and with further heating, the results are indicated in Fig. 111, but above 250° it is reduced to cobaltous

chloride; and when heated to constant weight in vacuo at 180°, the residue contains 2 mols. of the chloropentamminochloride, for 3 mols. of  $\text{NH}_4\text{Cl} \cdot \text{CoCl}_2 \cdot \frac{1}{2}\text{NH}_3$ .

The absorption spectrum was measured by W. F. Beyer, A. Gordienko, M. Chatalet-Lavollay, J. Kranig, R. Luther and A. N. Nikolopoulos, R. Samuel and co-workers, J. Angerstein, A. N. Nikolopoulos, C. Schleicher, Y. Shibata, and Y. Shibata and G. Urbain; the X-ray spectrum, by O. Stelling, and S. Aoyama and co-workers; and the Raman effect, by D. M. Bose and S. Datta, and I. Damaschun. R. Lorenz and I. Posen, and I. Posen gave for the equivalent electrical conductivity,  $\lambda$ , of a mol of the salt in *v* litres of water, at 25°:

$v$	32	64	128	256	512	1024
$\lambda$	124.6	135.9	147.9	155.7	163.9	169.9

and  $\lambda_\infty = 169.5$  mhos. W. D. Harkins and co-workers gave for soln. with *C* equivalents of the salt per litre at 0° and 25°:

<i>C</i>	0.1107	0.07722	0.05293	0.02015	0.002032	0.0004315
$\lambda$ { 0°	56.09	58.90	63.27	69.8	85.7	91.0
25°	101.3	109.2	117.2	130.2	160.0	172.0

Observations on the conductivity of the soln. were also made by G. R. Mines, A. Werner and A. Miolati, H. Ley, and J. Petersen. The results agree with the data on the lowering of the f.p. of the aq. soln. in that the ionization of the salt furnishes 4 ions per mol.:  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3 \rightleftharpoons [\text{Co}(\text{NH}_3)_2]^{3+} + 3\text{Cl}^-$ . The subject was discussed by A. Werner and C. Herty, and W. D. Harkins and co-workers. E. N. Gapon, R. Lorenz and I. Posen, and I. Posen found the transport number of the anion, at a dilution  $v=90$  per gram-equivalent, to be 0.430, 0.620, and 0.810, respectively, for 1, 2, or 3 chlorine atoms per mol.; and they gave for the mobility of the  $[\text{Co}(\text{NH}_3)_6]^{3+}$ -ion, 27.1 to 46.8. A. Bethe and T. Toropoff studied the electro-osmosis of the salt in soln.; and H. Freundlich and G. Ettisch, the electrokinetic potential at glass surfaces. A. B. Lamb and A. T. Larson measured the oxidation potentials of 6 cobaltic amines in soln. of ammonium hydroxide, and calculated the concentration of the  $\text{Co}^{3+}$ -ion in the mol. normal soln. of ammine. The oxidation potential of the hexamminochloride in 0.077*M*- $\text{NH}_4\text{OH}$  is 0.1558 volt. The order of stability, increasing onwards, is 1,6-dinitrotetrammine, hexammine, nitropentammine, 1,2-dinitropentammine, and aquopentammine. A. B. Lamb and A. T. Larson's value for the equilibrium constant in  $[\text{Co}(\text{NH}_3)_6]^{3+} \rightleftharpoons [\text{Co}^{3+}] + 6[\text{NH}_3]$ , is  $2.2 \times 10^{-34}$ . N. R. Dhar and G. Urbain found that the polarization tension of  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  decreases as the  $\text{NH}_3$ -mols. are replaced by

$\text{H}_2\text{O}$ -mols., whereas in the series  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ , the contrary holds good. The replacement of a molecule of water by a halogen in such a compound as  $\text{Co}(\text{NH}_3)_5\text{H}_2\text{OCl}_3$  causes a rise in the polarization tension. Further, in the purpureo-salts, the tension is higher when the purpureo-complex contains a more negative radicle. The replacement of a chlorine atom by a nitro-group, or of two chlorine atoms by a carbonato-group, causes a lowering of the polarization tension. The marked rise in the tension following on the substitution of an hydroxy-group for a chlorine atom is in agreement with the fact that these complex compounds are only stable in alkaline media. A. L. T. Moesveld and H. J. Hardon studied the electrostriction of the compound. E. Feytis gave for the magnetic susceptibility  $-0.38 \times 10^{-6}$  mass unit; and P. Pascal,  $-0.376 \times 10^{-6}$  mass unit. Observations on the magnetic properties were made by P. Collet, P. Weiss, E. Rosenbohm, D. M. Bose, L. C. Jackson, W. Biltz, and S. Berkman and H. Zocher. The co-ordination and structure were discussed by P. C. Ray; magnetic anisotropy, by L. W. Strock; the piezoelectric phenomena, by A. Hettich; and the electrostatic explanation of complex salt formation, by A. E. van Arkel and J. H. de Boer.

H. Lessheim and co-workers, F. Ephraim and W. Flügel, and F. Ephraim studied the bonding of the anions in salts of this type; J. A. V. Butler, T. M. Lowry, and C. H. Spiers, the electronic structure; and W. Biltz, A. B. Lamb and A. T. Larson, G. L. Clark and co-workers, J. A. N. Friend, and E. E. Turner, the constitution. P. Job examined the fractional precipitation of the three chlorides by soln. of silver nitrate. P. Mosimann and F. Ephraim gave 0.20 mol or 11.8 grms. per litre for the solubility of the salt in water; and observations were made by J. N. Bronsted and J. W. Williams. S. M. Jörgensen observed that the hexammine is very slowly hydrolyzed by boiling water; and R. Schwarz and co-workers observed that hydrolysis occurs at ordinary temp. in ultra-violet light. A. Benrath, and H. Pitzler studied the solubility of the salt in hydrochloric acid and water. E. Böhm observed that when a soln. of the hexamminochloride is treated with dil. hydrofluoric acid, brownish-yellow, prismatic crystals of **cobaltic hexamminofluodichloride**,  $[\text{Co}(\text{NH}_3)_6]\text{FCl}_2$ , are formed; the crystals effloresce in air or in vacuo; and they are freely soluble in hot water, but sparingly soluble in cold water and dil. acids. S. M. Jörgensen observed that with cold, sat. soln. of the ammine, the salt is precipitated by the addition of acids—dil. nitric acid, or conc. hydrochloric or hydrobromic acids; dil. sulphuric acid precipitates a sulphate; crystalline precipitates are produced by the addition of ammonium oxalate, sodium pyrophosphate, gold trichloride, and by potassium iodide, chromate, dichromate, ferrocyanide, ferricyanide, cobaltocyanide, and chromocyanide; iodine and potassium iodide give a black precipitate; ammoniacal sodium hydrophosphate gives a precipitate; mercuric chloride gives a precipitate only after hydrochloric acid has been added; and hydrochloroplatinic acid and sulphuric acid precipitate a double salt. F. Ephraim observed that when the well-cooled hexamminochloride is treated with ammonia gas or with liquid ammonia, cooled with solid carbon dioxide, **cobaltic dodecamminochloride**,  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3 \cdot 6\text{NH}_3$ , is formed. At  $-24^\circ$ , it loses  $3\text{NH}_3$  to form **cobaltic enneamminochloride**,  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3 \cdot 3\text{NH}_3$ ; between  $-12^\circ$  and  $-6^\circ$ , it forms a series of solid soln. with **cobaltic octamminochloride**,  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2 \cdot 2\text{NH}_3$ ; at  $-6^\circ$ , it passes into **cobaltic heptamminochloride**,  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3 \cdot \text{NH}_3$ ; and at  $24.5^\circ$  to  $30^\circ$ , it forms the hexammine. K. Matsuno, and H. Freundlich and H. Schucht studied the flocculation of arsenic sulphide sol by the hexammine; N. Schiloff and B. Nekrassoff, the reduction of the ammine, and the adsorption of soln. of the salt by activated charcoal; R. Schwarz and W. Krönig, the change of the hexammine to the chloropentammine by shaking the aq. soln. with charcoal, or silica-gel; F. Ephraim found that a 5 per cent. aq. soln. gives a precipitate with many substituted benzene and naphthalene substituted sulphonic acids.

For example, with 5-nitro-, 6-nitro-, and 7-nitro-naphthalene- $\alpha$ -sulphonic acids, 2 : 6-dinitro-*m*-xylene-4-sulphonic acid, 2 : 6-dinitrotoluene-4-sulphonic acid, 4 : 5-dichloro-2-nitrobenzenesulphonic acid, 2 : 5-dichlorobenzenesulphonic acid, 5-chloronaphthalene- $\alpha$ -sulphonic acid, 3 : 4-dichlorobenzenesulphonic acid, 4-chloro-2-nitrobenzenesulphonic acid, 2-chloro-3 : 5-dinitrobenzenesulphonic acid, *m*-nitrotoluene-4-sulphonic acid, *p*-nitrotoluene-2-sulphonic acid, dibromonaphthalene- $\beta$ -sulphonic acid, 1-nitronaphthalene-3 : 7-disulphonic acid, 1-nitronaphthalene-3 : 6-disulphonic acid,  $\beta$ -bromonaphthalenedisulphonic acid, naphthalene-1 : 6-disulphonic acid, naphthalene-1 : 5-disulphonic acid, naphthalene-2 : 7-disulphonic acid, 2 : 6-dinitrobenzene-1 : 4-disulphonic acid,  $\beta$ -naphthol-6 : 8-disulphonic acid (but not with benzene-*m*-disulphonic acid,  $\beta$ -naphthol-3 : 6-disulphonic acid, and 3 : 5-disulphobenzonic acid), with 7-chloronaphthalene-1 : 3 : 6-trisulphonic acid, 5-nitronaphthalene-1 : 3 : 7-trisulphonic acid (but not with naphthalene-1 : 3 : 6-trisulphonic acid or 7-chloronaphthalene 1 : 3 : 6-trisulphonic acid).

T. Hamburger examined the effect of the hexammine on chromate-gelatine; H. G. B. de Jong, the gelatinization of agar-agar sol; and E. Funk, the action of the ammine on catalase and amylase ferments.

G. R. Levi found that cobaltic hexamminochloride forms **copper cobaltic hexamminopentachloride**,  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3 \cdot \text{CuCl}_2$ ; F. Ephraim and P. Mosimann, brownish-red crystals of hydrated zinc cobaltic hexamminopentachloride,  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3 \cdot \text{ZnCl}_2 \cdot \text{H}_2\text{O}$ ; hydrated cadmium cobaltic hexamminopentachloride,  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3 \cdot \text{CdCl}_2 \cdot \text{H}_2\text{O}$ , in small, pale yellow crystals; and cadmium cobaltic hexamminoheptachloride,  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3 \cdot 2\text{CdCl}_2 \cdot 3\text{H}_2\text{O}$ , as a brownish-yellow, crystalline powder of sp. gr. 2.366 at 25°, when the sp. gr. of the anhydrous salt is 2.411 at 25°. The salt was also examined by F. Ephraim and O. Schütz, and E. Birk. S. M. Jörgensen reported orange-coloured microscopic crystals of **mercuric cobaltic hexamminopentachloride**,  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3 \cdot \text{HgCl}_2$ , which, according to F. Ephraim and O. Schütz, and E. Birk, have the sp. gr. 2.532 at 25°; J. M. Krok also described hydrated **mercuric cobaltic hexamminoheptachloride**,  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3 \cdot 2\text{HgCl}_2 \cdot 3\text{H}_2\text{O}$ , and S. M. Jörgensen, **mercuric cobaltic hexamminoenneachloride**,  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3 \cdot 3\text{HgCl}_2 \cdot 3\text{H}_2\text{O}$ . The complex salts with mercuric chloride were also studied by E. Carstanjen, G. Vortmann and E. Morgulis, Y. Shibata and T. Inoue, and T. Inoue. F. Ephraim and P. Mosimann prepared **mercuric cobaltic hexamminotrichloropentacyanide**,  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3 \cdot 5\text{HgCy}_2 \cdot \text{H}_2\text{O}$ . C. D. Braun reported **stannous cobaltic hexamminodecachloride**,  $2[\text{Co}(\text{NH}_3)_6]\text{Cl}_3 \cdot 3\text{SnCl}_2 \cdot n\text{H}_2\text{O}$ , and he obtained the *octohydrate*, and the *decahydrate*. E. Ephraim and P. Mosimann prepared pale yellow capillary needles of **lead cobaltic hexamminopentachloride**,  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3 \cdot \text{PbCl}_2$ ; and pale reddish-brown, 6-sided plates of **lead cobaltic hexamminoheptachloride**,  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3 \cdot 4\text{PbCl}_2$ . F. Ephraim and O. Schütz, and E. Birk found the sp. gr. to be 3.911 at 25°.

W. Feldt<sup>2</sup> prepared a **cobaltic hexahydroxylaminechloride**,  $[\text{Co}(\text{NH}_2\text{OH})_6]\text{Cl}_3$ , by the action of alcoholic hydrochloric acid on a suspension of cobaltous dihydroxylaminoychloride in alcohol, and strongly cooling the liquid; and A. Werner and E. Berl, by the action of a soln. of hydroxylamine chloride in potash-lye on cobaltic *trans*-dichlorobisethylenediaminochloride or on a soln. of cobaltic chlorohydroxylaminebisethylenediaminochloride. A. Fock found that the golden-yellow monoclinic crystals have the axial ratios  $a : b : c = 0.9358 : 1 : -$ , and  $\beta = 84^\circ 7'$ . According to A. Werner and E. Berl, the salt is stable towards hydrochloric acid, even during a prolonged boiling. The aq. soln. give a precipitate of the corresponding salt when it is treated with hydrobromic acid; a brown precipitate with hydriodic acid; and no precipitate with potassium iodide. Conc. sulphuric or nitric acid decomposes the salt at ordinary temp. No precipitate is formed when the soln. is treated with ammonium sulphate, sodium dithionate, potassium dichromate, mercuric chloride, or hydrochloroplatinic acid; there is a yellow or brown precipitate with potassium cyanide, ferrocyanide, or ferricyanide, sodium carbonate or acetate, or ammonium oxalate. The salt is not acted on by acetyl chloride; but boiling anhydrous acetic acid reduces it to a cobaltous salt; and benzaldehyde and salicylaldehyde form complex products. C. S. Borzekowsky prepared **cobaltic hydroxylaminebisethylenediamineamminochloride**,  $[\text{Co}(\text{NH}_3)_2\text{en}_2(\text{NH}_2\text{OH})]\text{Cl}_3$ , both in the dextro- and lævo-forms.

S. M. Jörgensen<sup>3</sup> obtained **cobaltic trisethylenediaminechloride**,  $[\text{Co en}_3]\text{Cl}_3$ , by oxidizing a soln. of cobaltous chloride in ethylenediamine. The salt was also prepared by H. Grossmann and B. Schück, and L. L. Lehrfeld. The air-dried salt is the *trihydrate*, which becomes anhydrous over sulphuric acid, or at 100°.

M. Delépine and R. Charonnet obtained optically-active compounds of the chloride. F. M. Jäger found that the ditrigonal crystals have the axial ratio  $a : c = 1 : 0.6667$ ; the sp. gr. 1.542 at  $17^\circ$ ; the mol. vol. 295.08; and the topic axial ratio  $\frac{1}{2}\psi : \omega = 4.2129 : 5.6175$ . R. Lorenz and I. Posen, and I. Posen calculated the sp. gr. in vacuo to be 1.5132, and the mol. vol. at absolute zero 233.8. E. N. Gapon studied the diffusion. A. Benrath and W. Kohlberg, and A. G. Bergmann measured the vap. press. and obtained indications of a *monohydrate*. H. Grossmann and B. Schück gave  $256^\circ$  for the m.p. Y. Shibata, R. Samuel and co-workers, Y. Shibata and G. Urbain, C. Schleicher, F. W. Beyer, A. Mead, and J. Angerstein measured the absorption spectra of aq. soln. G. Berger studied the photochemical decomposition of the salt. R. Lorenz and I. Posen found the equivalent conductivity,  $\lambda$ , for soln. of  $v$  litres per gram-equivalent, at  $25^\circ$ :

$v$	62	128	256	152	1024
$\lambda$	110.2	119.3	127.3	133.6	137.8

and at infinite dilution,  $\lambda_\infty = 142.8$ . A. Werner and C. Herty measured the mol. conductivity. R. Lorenz and I. Posen gave 0.512 for the transport number of the anion for  $v=192$  at  $20^\circ$ ; and E. N. Gapon studied the subject. E. Rosenbohm found the magnetic susceptibility to be  $-4.90 \times 10^{-7}$  mass unit. A. Rostkowsky found for the solubility,  $S$  mols. per cent.:

$S$	$10^\circ$	$20.3^\circ$	$30^\circ$	$50^\circ$	$70^\circ$	$90^\circ$	$110^\circ$
	1.2	1.6	2.1	3.2	4.5	5.9	7.3

According to S. M. Jörgensen, with a 2 per cent. aq. soln., conc. nitric or hydrochloric acids give no precipitate; and conc. hydrobromic acid gives an incomplete precipitation; soln. of potassium iodide give no precipitate, but a soln. of iodine and potassium iodide gives a dark brown, crystalline precipitate. Yellowish- or reddish-brown precipitates are produced by mercuric chloride, sodium chloroplatinate, gold chloride, or potassium chloroplatinite, ferrocyanide or ferricyanide (with a few drops of dil. hydrochloric acid). When the aq. soln. is evaporated with nitric acid, the nitrate of the series is formed; nitrous acid has no action; boiling, 7 per cent. soda-lye does not decompose the salt; and ammonium sulphide does not give an immediate precipitation. G. and P. Spacu prepared **mercury cobaltic trisethylenediaminobichlorides**,  $[\text{Co en}_3](\text{HgCl}_2)_3$ , and  $[\text{Co en}_3]_2(\text{HgCl}_4)_3$ ; **bismuth cobaltic trisethylenediaminechloride**,  $[\text{Co en}_3](\text{BiCl}_6) \cdot 2\text{H}_2\text{O}$ .

According to A. Werner, there are two possible salts of triethylenediaminecobalt which stand to each other in the relation of object and mirror-image, and are not superposable. These may be represented as in Fig. 111. Such compounds form the simplest possible case of molecular asymmetry, being specially characterized by having all the co-ordination positions of the central atom occupied by structurally identical groups, the asymmetry being caused by the special spatial arrangement of these groups. This type of isomerism can be called *molecular asymmetry*. A. Werner prepared the *dextro-salt*, and the *laevo-salt*. If the aq. soln. of the optically active bromide of the series (*q.v.*) be shaken with freshly precipitated silver chloride, the filtrate evaporated, and then treated with alcohol, golden-yellow needles of the corresponding optically active cobaltic trisethylenediaminobichloride are formed. A. Werner found the sp. rotation of a 1 per cent. soln. for yellow- and red-light is  $[\alpha] = 152^\circ$  for the dextrorotatory form, and  $-154^\circ$  for the laevorotatory form. E. Rosenbohm gave  $-4.54 \times 10^{-7}$  for the magnetic susceptibility of the two forms. Measurements were also made by L. C. Jackson.

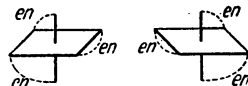


FIG. 112.—A. Werner's Molecular Asymmetry.

J. Meisenheimer and co-workers prepared hydrated **sodium cobaltic trisethylenediamineheptachloride**,  $2[\text{Co en}_3]\text{Cl}_3 \cdot \text{NaCl} \cdot 6\text{H}_2\text{O}$ , in yellowish-brown prisms from the chloride of the series mixed with soln. of sodium chloride; N. S. Kurnakoff likewise obtained hydrated **copper cobaltic trisethylenediaminopentachloride**,  $[\text{Co en}_3]\text{Cl}_3 \cdot \text{CuCl}_2 \cdot \text{H}_2\text{O}$ , in yellowish-

brown plates, sparingly soluble in water acidified with hydrochloric acid. The water of crystallization is given off at  $112^\circ$ , not at  $100^\circ$ . A. Werner and F. Bräunlich prepared **cobaltous cobalt trisethylenediaminooctachloride**,  $2[\text{Co en}_3]\text{Cl}_3 \cdot \text{CoCl}_2 \cdot 4\text{H}_2\text{O}$ , from a boiling soln. of the chloride of the series and an excess of cobalt chloride, acidified with hydrochloric acid. The emerald-green needles or prisms are decomposed by water. No water is lost over sulphuric acid, but all is lost at  $110^\circ$ . N. S. Kurnakoff prepared hydrated **cobaltous cobaltic trisethylenediaminepentachloride**,  $[\text{Co en}_3]\text{Cl}_3 \cdot \text{CoCl}_2 \cdot 5\text{H}_2\text{O}$ , by evaporating on a water-bath a soln. of 1 part of the chloride of the series, and 1 to 2 parts of cobaltous chloride. The brownish-violet liquid furnishes dark green needles or prisms. A. G. Bergmann also prepared **nickel cobaltic trisethylenediaminooctachloride**,  $2[\text{Co en}_3]\text{Cl}_3 \cdot \text{NiCl}_2$ .

P. Pfeiffer and T. Gassmann treated cobaltic chloropentamminochloride with propylenediamine monohydrate and obtained yellow, non-crystalline **cobaltic trispropylenediaminooctachloride**,  $[\text{Co pn}_3]\text{Cl}_3$ , when pn stands for  $\text{C}_3\text{H}_5(\text{NH}_2)_2$ . F. M. Jäger and H. B. Blumendal prepared small, blood-red crystals of **cobaltic tritranscyclopentanediaminooctachloride**,  $[\text{Co}(\text{C}_5\text{H}_9\text{N}_2)_3]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$  by the action of transcyclopentanediamine on cobaltic dichloroditranscyclopentanediaminooctachloride. The triclinic crystals have the axial ratios  $a : b : c = 2.2474 : 1 : 1.5625$ . By the action of the active tartratochloride of the series on the active iodide, the *trihydrate* of the optically active salt is produced in hexagonal pyramids with the axial ratio  $a : c = 1 : 2.5328$ , and sp. gr. 1.364 at  $20^\circ$ . The *tetrahydrate* forms regular crystals. F. M. Jäger and H. B. Blumendal obtained the optically active **cobaltic tris-cyclopentanediaminooctachloride**, in brick-red, octahedral crystals, by the action of *l*-cyclopentanediamine on cobaltic chloropentamminochloride. The *trihydrate*, and *tetrahydrate* were prepared. F. G. Mann and W. J. Pope heated on a water-bath a soln. of triaminopropanetrihydrochloride in 15 per cent. soda-lye with cobaltic chloropentamminochloride or aquopentamminochloride, and obtained optically inactive **cobaltic tris-triaminopropanechloride**,  $[\text{Co}\{\text{C}_3\text{H}_5(\text{NH}_2)_3\}_3]\text{Cl}_3$ , in orange-red needles which melt at  $312^\circ$  to  $314^\circ$  with decomposition; they are soluble in water. The optically active *dextro-salt* was obtained from the  $\alpha$ -camphor- $\beta$ -sulphonate of the series.

A. Werner prepared **cobaltic cis-bisethylenediaminediamminooctachloride**,  $[\text{Co en}_2(\text{NH}_3)_2]\text{Cl}_3$ , by treating with perhydrol and hydrochloric acid, a soln. of a salt of cis-bisethylenediaminodithiocyanatoammine, and evaporating the liquid. R. Plischke prepared **cobaltic bisethylenediaminepyridineamminooctachloride**,  $[\text{Co}(\text{NH}_3)_2\text{py}]\text{Cl}_3$ . Optically active forms were prepared by A. Werner and Y. Shibata from the *l*-bromo camphor sulphonate. The golden-yellow crystals of the *dextro-salt* have  $[\alpha] = 50^\circ$  and  $15^\circ$  for yellow- and red-light, and the *lævo-salt*,  $-51^\circ$  and  $-16^\circ$ . A. Werner and C. Kreutzer obtained **cobaltous cobaltic cis-bisethylenediaminediamminopentachloride**,  $[\text{Co en}_2(\text{NH}_3)_2]\text{Cl}_3 \cdot \text{CoCl}_2$ . A. Werner and co-workers, W. Tupizina, and K. R. Lange prepared **cobaltic trans-bisethylenediaminediamminooctachloride**,  $[\text{Co en}_2(\text{NH}_3)_2]\text{Cl}_3 \cdot \text{H}_2\text{O}$ , by oxidizing the trans-form of salt employed in preparing the cis-modification. The salt furnishes amber-yellow, thick plates, stable in air; H. Grossmann and B. Schick said that the pale yellow, needle-like crystals effloresce in air. F. M. Jäger and co-workers said that the monoclinic prisms have the axial ratios  $a : b : c = 2.7565 : 1 : 1.3677$ , and  $\beta = 101^\circ 48'$ , and have no perceptible cleavage. The sp. gr. is 1.659 at  $17^\circ$ ; the mol. vol. 203.43; and the topic axial ratios  $\chi : \psi : \omega = 10.4930 : 3.8058 : 5.2052$ . R. Lorenz and I. Posen gave 1.6426 for the sp. gr. reduced to a vacuum, and for the anhydrous salt they gave 1.644. H. Grossmann and B. Schick gave  $252^\circ$  for the m.p. C. Schleicher, A. Gordienko, and Y. Shibata and G. Urbain studied the absorption spectrum. R. Lorenz and I. Posen found the eq. conductivity,  $\lambda$ , for a gram-equivalent of the salt, in litres, at  $25^\circ$ :

$v$	.	.	.	64	128	256	512	1024
$\lambda$	.	.	.	117.1	126.5	134.7	141.4	147.7

and for infinite dilution  $\lambda_\infty = 149.9$ . Measurements were also made by A. Werner and C. Herty. R. Lorenz and I. Posen found the transport number of the anion to be 0.496 at  $19^\circ$  when  $v = 90$ . A. Werner and co-workers found that nitric acid, hydrobromic acid, and potassium iodide precipitate the corresponding salt of the series; whilst hydrochloroplatinic acid, gold chloride, mercuric chloride, stannous chloride and hydrochloric acid, and potassium chloroplatinite gave a dark yellow, crystalline precipitate. A. Werner and co-workers also prepared **gold cobaltic bisethylenediaminediamminoenechloride**,  $[\text{Co}(\text{NH}_3)_2\text{en}_2]\text{Cl}(\text{AuCl}_4)_2$ , and **gold cobaltic bisethylenediaminediamminohexachloride**,  $[\text{Co}(\text{NH}_3)_2\text{en}_2]\text{Cl}_2(\text{AuCl}_4)_2$ , in yellow plates; **mercuric cobaltic trans-bisethylenediaminediamminotridecachloride**,  $[\text{Co en}_2(\text{NH}_3)_2]\text{Cl}_3 \cdot 5\text{HgCl}_2$ , in yellow, needle-like crystals; and **hydrated cobaltous cobaltic transbisethylenediaminediamminopentachloride**,  $[\text{Co en}_2(\text{NH}_3)_2]\text{Cl}_3 \cdot \text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ , in thin plates which are brownish-red in transmitted light, and dark green, almost black, in reflected light.

A. Werner and K. Dawe prepared **cobaltic bispropylenediaminediamminooctachloride**,  $[\text{Co pn}_2(\text{NH}_3)_2]\text{Cl}_3$ , by passing chlorine into a soln. of a salt of cobaltic dithiocyanatobispropylenediaminooctachloride. The golden yellow, 6-sided prisms are very soluble in water, but the addition of alcohol or ether precipitates the salt from the aq. soln. Hydrochloric acid does not precipitate the chloride from the aq. soln. Hydrobromic, or nitric

acid, potassium bromide or iodide, and sodium dithionate precipitate the corresponding salt from the aq. soln.; potassium dichromate, ferrocyanide or ferricyanide, gold chloride, mercuric chloride or stannous chloride and hydrochloric acid give pale yellow or reddish-yellow, crystalline precipitates; picric acid gives a lemon-yellow precipitate; potassium permanganate, yellow plates; and cobaltous chloride, a green double salt; whilst ferrous chloride, cuprous chloride, zinc chloride, ammonium oxalate, sodium hydrophosphate, and sodium acetate give no precipitates. Needle-like or prismatic crystals of **mercuric cobaltic bispropylenediaminediamminoheptachloride**,  $[\text{Co pn}_2(\text{NH}_3)_2]\text{Cl}_3 \cdot 2\text{HgCl}_2$ , were prepared; also yellowish-red crystals of **stannous cobaltic bispropylenediaminediamminoheptachloride**,  $[\text{Co pn}_2(\text{NH}_3)_2]\text{Cl}_3 \cdot 2\text{SnCl}_2$ ; and pale green plates of hydrated **cobaltous cobaltic bispropylenediaminediamminopentachloride**,  $[\text{Co pn}_2(\text{NH}_3)_2]\text{Cl}_3 \cdot \text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ . W. A. Re-deker prepared **cobaltic pyridinebisethylenediamineamminochloride**,  $[\text{Co}(\text{NH}_3)_2\text{en}_2\text{py}]\text{Cl}_3$ .

F. M. Jäger and H. B. Blumendal prepared **cobaltic ethylenediaminebis-cyclopentanediaminechloride**,  $[\text{Co en}(\text{C}_5\text{H}_{12}\text{N}_2)_2]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ , by heating cobaltic trans-dichlorobis-cyclopentanediaminechloride with a 10 per cent. soln. of ethylenediamine. They also prepared **cobaltic bisethylenediamine-trans-cyclopentanediaminechloride**,  $[\text{Co en}_2(\text{C}_5\text{H}_{12}\text{N}_2)]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ , by heating cobaltic dichlorobisethylenediaminechloride, or aquochlorobisethylenediaminechloride with cyclopentanediamine; and also **cobaltic bisethylenediamine-l-cyclopentanediaminechloride** by heating cobaltic dichlorobisethylenediaminechloride with l-cyclopentanediamine. F. M. Jäger and P. Koets prepared **cobaltic sexiesethylenediamine-bistriaminotriethylamine-enneachloride**,  $[\text{Co}_3\text{en}_6(\text{C}_6\text{H}_{18}\text{N}_3)_2]\text{Cl}_3 \cdot 4\text{H}_2\text{O}$ , by the action of triaminotriethylamine on a soln. of cobaltic aquochlorobisethylenediaminechloride. C. J. Dippel and F. M. Jäger prepared **cobaltic trisdiaminopentanochloride**,  $[\text{Co ptn}_3]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ , with  $\alpha\beta\delta$ - and  $\beta\beta\delta$ -diaminopentanes.

O. W. Gibbs and F. A. Genth<sup>4</sup> prepared **cobaltic roseochloride**, **cobaltic aquo-pentamminochloride**,  $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]\text{Cl}_3$ , by oxidizing an ammoniacal soln. of cobaltous chloride in air, and adding hydrochloric acid to the cold liquid. If the warm soln. is treated with hydrochloric acid, cobaltic chloropentamminochloride is precipitated, but if the acid be added slowly, and the soln. be kept very cold, the aquopentamminochloride is deposited. J. M. Krok oxidized the soln. with chlorine; and E. J. Mills, with permanganate. F. Rose recommended shaking a cobaltic chloropentamminochloride with hot, 5 per cent., aq. ammonia, and dropping the cold liquid into an equal vol. of conc. hydrochloric acid; and a similar process was employed by A. Benrath, N. R. Dhar, and R. Pers; S. M. Jörgensen, and O. W. Gibbs used the nitratopentamminonitrate in place of the chloro-salt; and S. M. Jörgensen, and O. Hassel and J. R. Salvesen, the oxalato-salt. H. and W. Biltz thus describe the preparation of this salt:

A cold soln. of 20 grms. of hydrated cobalt chloride in 360 c.c. of water, in a 1500-c.c. flask, is mixed with 110 c.c. of conc. aq. ammonia, and then with 10 grms. of potassium permanganate dissolved in 400 c.c. of water. The mixture is well agitated, and after standing 24 hrs., it is filtered to remove the hydrated manganese dioxide. The filtrate is neutralized with dil. hydrochloric acid, and, while keeping it cold with ice, a mixture of 3 vols. of hydrochloric acid and 1 vol. of alcohol is added. The precipitate is washed with alcohol; the yield is 10 grms. The crude product is then dissolved in cold, 2 per cent. aq. ammonia, using 75 c.c. for each 10 grms. of salt. Filter off the slight residue of the hexamminochloride, and, whilst keeping the soln. cold with ice, gradually add conc. hydrochloric acid. Drain the precipitate, wash it with a 1:1 mixture of hydrochloric acid and water, then with alcohol, and dry the product in a warm place.

The crystalline powder is brick-red and dichroic. H. V. Arny and C. H. Ring recommended an ammoniacal 0.1N-soln. as a standard in comparing red colour tints. F. Ephraim and O. Schütz found the sp. gr. to be 1.743 at 25°, and the mol. vol. 154.1. There is a vol. contraction of 67 per cent. during the formation of the salt. E. Birk found for the sp. gr. 1.745 at 25°/4°, and for the mol. vol. 153.8. R. Lorenz and I. Posen, and I. Posen gave 1.7629 for the sp. gr. reduced to a vacuum. G. L. Clark and co-workers gave 1.776 for the sp. gr., 151.29 for the mol. vol., 16.20 for the mol. vol. of the contained  $\text{NH}_3$ -groups, and 14.05 for the contained  $\text{H}_2\text{O}$ -group. J. Petersen calculated the mol. wt., 226, from the f.p. of aq. soln. of the salt. J. N. Brønsted and K. Volquartz studied the ionization. O. W. Gibbs and F. A. Genth, and A. Werner observed that the solid salt slowly changes into cobaltic chloropentamminochloride, and A. B. Lamb and J. W. Marden added that the transformation is irreversible and is attended by the loss of a mol. of water.

At 25°, the water vapour of aquopentamminochloride has a critical press. of 5.1 mm. The solid salt is not a stable phase at 25° in water or in hydrochloric acid. The transformation of the aquopentammine into chloropentammine in aq. soln. was studied by O. W. Gibbs and F. A. Genth, and E. J. Mills. A. Benrath and K. Mienes observed that the transformation proceeds more slowly as the concentration of the hydrochloric acid increases. A. B. Lamb and J. W. Marden found that in aq. soln., in soln. containing chlorides, and in hot, dil. hydrochloric acid soln., a state of equilibrium is attained; at 70°, a 0.02*M*-soln. of the aquo-pentammine or chloropentammine in the presence of 0.02*M*-HCl, contains 70.5 per cent. of the aquopentammine, and in the presence of 0.1*M*-HCl, 65 per cent. in 20 hrs. no matter which salt is employed at the start. R. Pers said that in boiling, dil. hydrochloric acid, the equilibrium constant,  $K=1.4$ , corresponding with 58 per cent. of the aquopentammine, and 42 per cent. of the chloropentammine. P. Job observed that in alkaline soln., the aquopentammine passes quantitatively into the hydroxypentammine. A. B. Lamb and A. T. Larson studied the relative stability of soln. of many of the amines—*vide supra*, hexamminochloride. A. B. Lamb and J. P. Simmons gave  $-6.46$  Cals. for the mol. heat of solution in water at 25°. The absorption spectra of aq. soln. were studied by A. N. Nikolopulos, R. Luther and A. N. Nikolopulos, Y. Shibata, Y. Shibata and G. Urbain, and E. Valla; and the X-ray spectrum, by F. de Boer. A. Werner and A. Miolati measured the mol. conductivity,  $\mu$ , at 25°, and found for a mol of the salt in *v* litres:

<i>v</i> . . . .	128	256	5.12	1024	2048
$\mu$ . . . .	330.6	354.7	381.4	393.7	410.4

R. Lorenz and I. Posen measured the eq. conductivity; and J. Petersen obtained for a gram-equivalent of the salt in *v* litres, the following values for the degree of ionization,  $\alpha$ , and for the factor *i* or *n* (1, 15, 10):

<i>v</i> . . . .	1	2	5	10	50	100	1000
$\alpha$ . . . .	0.55	0.62	0.66	0.73	0.79	0.86	0.97
<i>i</i> . . . .	2.65	2.86	2.98	3.19	3.37	3.58	3.91

A. B. Lamb and A. T. Larson studied the oxidation potential, and N. R. Dhar and G. Urbain, the polarization tension—*vide supra*, the hexamminochloride. O. W. Gibbs and F. A. Genth observed that the boiling of a neutral soln. is attended by the deposition of cobaltous hydroxide; and A. B. Lamb and J. W. Marden, that the soln. feebly acidified with hydrochloric acid is slowly hydrolyzed at 100°; and R. Schwarz and co-workers, that an aq. soln. at ordinary temp. is hydrolyzed when exposed to ultra-violet rays. N. R. Dhar and G. Urbain measured the polarization tension—*vide supra*, the hexamminochloride. H. Moehle studied the magnetic properties of the salt.

N. S. Kurnakoff found that 100 parts of water dissolve 16.2 parts of cobaltic aquopentamminochloride at 0°, and 24.87 parts at 16.9°; and F. Ephraim observed that a sat. soln. at 17.5° contains 0.859 mol per litre. S. M. Jörgensen observed that the addition of sulphuric acid gives no precipitate, and he observed no reaction with dil. hydrochloric or hydrobromic acid, sodium dithionate, and hydrophosphate. F. Ephraim found that a current of ammonia acts on the salt at  $-21^\circ$ , forming a purple-red **cobaltic aquohenamminochloride**,  $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]\text{Cl}_3.6\text{NH}_3$ , which, at  $-8.5^\circ$ , furnishes a bluish-red powder of **cobaltic aquooctamminochloride**,  $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]\text{Cl}_3.3\text{NH}_3$ , and as the temp. rises, this product passes into **cobaltic aquoheptamminochloride**,  $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]\text{Cl}_3.2\text{NH}_3$ , which, as the temp. rises to  $38.5^\circ$ , passes into **cobaltic aquohexamminochloride**,  $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]\text{Cl}_3.\text{NH}_3$ , and this red salt is stable up to  $66^\circ$ . H. Freundlich and H. Schucht observed that a sol. of arsenic trisulphide is flocculated by cobaltic aquopentamminochloride. A. B. Lamb and J. P. Simmons gave  $-6460$  cal. for the mol. heat of soln. J. N. Brönsted and K. Volquartz studied the effect of the salt on the decomposition

of nitramide; and J. N. Brönsted, the behaviour of the salt in acid and base catalysis. S. M. Jörgensen, O. W. Gibbs and F. A. Genth, and E. J. Mills found that a soln. of cobaltic aquopentamminochloride gives no precipitate with hydrofluosilicic acid, but it gives yellowish-red precipitates with potassium iodide, ammonium oxalate, potassium chromate or dichromate, chloroaurate, and ferrocyanide, or with sodium pyrophosphate. P. Job found that all the chloride is precipitated by silver nitrate from aq. soln. of the salt.

O. W. Gibbs reported gold cobaltic aquopentamminohexachloride,  $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]\text{Cl}_2(\text{AuCl}_4)$ , in orange-red crystals, by the action of sodium chloroaurate on a soln. of the aquopentamminochloride; F. Ephraim and co-workers obtained zinc cobaltic aquopentamminopentachloride,  $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]\text{Cl}_3\cdot\text{ZnCl}_2$ , as a red salt from a soln. of 1 mol. of the aquopentammine acid, and 10 mols. of zinc chloride; also cadmium cobaltic aquopentamminohexachloride,  $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]\text{Cl}_3\cdot 2\text{CdCl}_2\cdot 3\text{H}_2\text{O}$ , as a pale rose-red, crystalline powder of sp. gr. 2.434 at 25°, and mol. vol. 283, which corresponds with a contraction of 57 per cent. in the formation of the salt. The subject was studied by E. Birk. S. M. Jörgensen prepared mercuric cobaltic aquopentamminopentachloride,  $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]\text{Cl}_3\cdot\text{HgCl}_2$ , by adding mercuric chloride to a strongly acidic soln. of the aquopentammine. By re-crystallization from aq. soln., mercuric cobaltic aquochloropentamminooctachloride,  $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]\text{Cl}_3\cdot 3\text{HgCl}_2\cdot \text{H}_2\text{O}$ , is formed, and also, along with a double salt, with chloropentamminochloride,  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_3\cdot 3\text{HgCl}_2$ , by treating a boiling, feebly acidic soln. of chloropentamminochloride, with a hot soln. of mercuric chloride, and subsequently separating the two double salts by fractional crystallization. The salt was also prepared by O. W. Gibbs. It furnishes violet prisms. It is decomposed by cold, conc. hydrochloric acid, and it loses all its water at 100°. E. Carstanjen reported a pentahydrate, but this was not confirmed by O. W. Gibbs, or S. M. Jörgensen.

S. M. Jörgensen treated an ice-cold, 20 per cent. soln. of cobaltic carbonatetetramminochloride with dil. hydrochloric acid, and then with conc. hydrochloric acid, thereupon, cobaltic diaquotetramminochloride,  $[\text{Co}(\text{H}_2\text{O})_2(\text{NH}_3)_4]\text{Cl}_3$ , is deposited in small, dark red, octahedral crystals. E. Birk also prepared the salt in this manner, and A. Werner, by the action of cold conc. hydrochloric acid on a dodecammino-hexahydroxy-salt, or an octamminodihydroxy-salt. G. Vortmann reported a monohydrate to be formed by adding hydrochloric acid to an oxidized ammoniacal soln. of cobalt carbonate. E. Birk, and W. Biltz found the sp. gr. to be 1.783 at 25°/4°, and the mol. vol. 151.1. R. Lorenz and I. Posen, and I. Posen calculated 1.8363 for the sp. gr. in vacuo. According to S. M. Jörgensen, when the salt is heated to 100°, it passes into aquochlorotetramminochloride; and A. Werner added that the same change occurs very slowly at ordinary temp. J. N. Brönsted and K. Volquartz studied the ionization of the salt. A. Benrath and K. Andreas observed that the solid is not stable in contact with a sat. aq. soln., or dil. hydrochloric acid soln., but passes into the chloro-aquotetrammine, and this the more slowly, the more concentrated is the acid. P. Job found that in contact with barium hydroxide, the  $2\text{H}_2\text{O}$ -groups are replaced by two OH-groups. A. B. Lamb and A. T. Larson studied the stability of the salt in ammoniacal soln.—*vide supra*, the hexamminochloride. The absorption spectra were studied by A. N. Nikolopulos, R. Luther and A. N. Nikolopulos, Y. Shibata, Y. Shibata and G. Urbain, K. Matsuno, and E. Valla. R. Lorenz and I. Posen, and I. Posen found the equivalent conductivity,  $\lambda$ , for soln. with a gram-equivalent in  $v$  litres at 0.6°:

$v$	.	.	.	64	128	256	512	1024
$\lambda$	.	.	.	54.37	57.70	61.08	64.30	66.77

and at the limit,  $\lambda_\infty = 71.6$ . R. Schwarz and K. Tede noted that the salt in aq. soln. is hydrolyzed on exposure to ultra-violet rays. A. B. Lamb and A. T. Larson studied the oxidation potential; and N. R. Dhar and G. Urbain, the polarization tension—*vide supra*, the hexamminochloride. F. Ephraim found that a sat. aq. soln. at 22° contains 1.83 mols per litre; and A. Benrath and K. Andreas noted that the solubility is 3.83, which drops to 0.20 when 29.08 per cent. hydrochloric acid is present. A. Werner found that in dil. acetic acid soln., pyridine forms a complex dodecammine. J. N. Brönsted and K. Volquartz studied the effect of the



salt on the decomposition of nitramide. G. Vortmann prepared **mercuric cobaltic diaquotetramminochloride**.

A. Werner and co-workers, and J. D. Dubsky prepared hydrated **cobaltic cis-diaquobisethylenediaminechloride**,  $[\text{Co en}_2(\text{H}_2\text{O})_2]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ , by hydrating cis-dichlorobisethylenediaminechloride; by the action of hydrochloric acid on sexesethylenediaminehexahydroxy-nitrate, or on quaterethylenediaminetetrahydroxysulphate. The compound passes into violet dichlorobisethylenediaminechloride on keeping; it loses 4 mols. of water in vacuo over phosphorus pentoxide, or at  $115^\circ$ , so as to form the violet dichlorobisethylenediaminechloride. It forms a yellowish-red soln. with water. K. Matsuno, and A. Uspensky and K. Tschibisoff studied the absorption spectrum. According to A. Werner, when the salt is treated with dil. potash-lye, brownish-red  $[\text{Co en}_2(\text{H}_2\text{O})(\text{OH})]\text{Cl}_2$  is formed; with sodium nitrite,  $[\text{Co en}_2(\text{NO}_2)(\text{NO}_2)]$  is formed. A. Werner and co-workers also prepared hydrated **cobaltic trans-diaquobisethylenediaminechloride**,  $[\text{Co en}_2(\text{H}_2\text{O})_2]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ , by the action of conc. hydrochloric acid on cobaltic trans-aquohydroxybisethylenediaminebromide. It passes into the violet form of dichlorobisethylenediaminechloride on keeping, and if a trace of acid is present, the green form. K. Matsuno, and A. Uspensky and K. Tschibisoff studied the absorption spectra. A. Werner prepared **cobaltic diaquodipyridinediamminochloride**,  $[\text{Co}(\text{NH}_3)_2(\text{H}_2\text{O})_2\text{py}_2]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ , by the action of conc. hydrochloric acid on the aquohydroxydipyridinediamminochloride.

A. Werner prepared **cobaltic cis-triaquotriamminochloride**,  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_3]\text{Cl}_3$ , by allowing a trinitratotriammino-salt to stand for 24 hrs. in contact with acetic acid, and adding hydrochloric acid, saturated at  $0^\circ$ , to the ice-cold filtered liquid. The pale violet, crystalline powder is separated quickly, since if allowed to stand in contact with the mother-liquor, it changes into dichloroatriamminochloride. E. Birk, and W. Biltz gave 1.8114 for the sp. gr. at  $25^\circ/4^\circ$ , and 149.1 for the mol. vol. N. R. Dhar and G. Urbain studied the polarization tension—*vide supra*, the hexamminochloride; J. N. Brönsted and K. Volquartz, the ionization; R. Schwarz and K. Tede, the hydrolysis of the aq. soln. by exposure to ultra-violet rays; K. Matsuno, the absorption spectrum; J. N. Brönsted and K. Volquartz, the effect of the salt on the decomposition of nitramide; H. Freundlich and H. Schucht, the flocculation of a sol of arsenic sulphide by the salt; and A. Werner, the precipitation of the chloride-ions by soln. of silver nitrate. By evaporating an aq. soln. of cobaltic dichloroatriamminochloride in water acidified with hydrochloric acid, the soln. changes from bluish-violet to reddish-violet as it forms the isomeric **cobaltic trans-triaquotriamminochloride**. The absorption spectrum was studied by K. Matsuno. The dissociation tension of **cobaltic tetraquodiamminochloride**,  $[\text{Co}(\text{NH}_3)_2(\text{H}_2\text{O})_4]\text{Cl}_3$ , was studied by N. R. Dhar and G. Urbain, and the ionization by J. N. Brönsted and K. Volquartz.

#### *The CoA<sub>5</sub> or Pentammine Family.*

In 1851, F. Claudet,<sup>5</sup> and F. A. Genth described the first of the pentammine series of cobaltic chlorides. F. Claudet's analysis gave  $\text{CoN}_5\text{H}_{16}\text{Cl}_3$ , and E. Frémy's,  $\text{CoN}_5\text{H}_{15}\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ , but the analysis of W. Gregory, B. J. Rogojsky, and O. W. Gibbs and F. A. Genth agreed that the composition is correctly represented by  $\text{CoN}_5\text{H}_{15}\text{Cl}_3$ ; and the work of S. M. Jörgensen, A. Werner, J. A. N. Friend, and E. E. Turner indicated that, constitutionally, the compound is **cobaltic chloropentamminochloride**,  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ . F. Claudet, and F. A. Genth prepared the salt by oxidizing, with air or oxygen, an ammoniacal soln. of cobaltous and ammonium chlorides, and precipitating the product with hydrochloric acid. E. J. Mills employed potassium permanganate as oxidizing agent, and C. D. Braun, indigo-blue in a boiling soln. The salt was prepared, by these methods, by J. M. Krok, C. Künzel, B. J. Rogojsky, H. Schiff, A. Terreil, and W. D. Harkins and co-workers. J. H. Buckminster and E. F. Smith oxidized the ammoniacal soln. of cobaltous chloride, in the presence of ammonium sulphate and potassium chromate, electrolytically, and then precipitated the salt by the addition of hydrochloric acid. O. W. Gibbs and F. A. Genth prepared the salt by boiling cobaltic aquopentammine nitrate, or nitroxylpentamminonitrate, with hydrochloric acid; and W. Biltz,

by heating cobaltic hexamminochloride at  $225^{\circ}$ , in a current of ammonia. H. and W. Biltz, S. P. L. Sörenson, and W. D. Harkins and co-workers proceed somewhat as follows :

A cold, filtered soln. of 20 grms. of cobaltous carbonate in as little hydrochloric acid as possible, is treated with 250 c.c. of 10 per cent. ammonia, and 50 grms. of ammonium carbonate in 250 c.c. of water. Air is passed through the mixture for 3 hrs. and then 150 grms. of ammonium chloride are added and the soln. evaporated on a water-bath to a syrupy liquid. The mixture is then acidified with hydrochloric acid to drive off the carbon dioxide, the acid is neutralized with ammonia, and 10 c.c. of conc. ammonia in excess are added. Dilute the mixture to 400 or 500 c.c., and warm the soln. on a water-bath for one hour. Add 300 c.c. of conc. hydrochloric acid, and allow the soln. to stand on a water-bath for 30 to 45 minutes. The crystals are then filtered off from the cold liquid and washed with dil. hydrochloric acid. The salt can be purified by digesting it in 300 c.c. of a 2 per cent. soln. of ammonia, extracting the residue twice with 50 c.c. of the same ammonia soln., and precipitating the salt by adding 300 c.c. of conc. hydrochloric acid, and keeping the mixture on a water-bath for about 45 minutes. When cold, the soln. is filtered, and the precipitate washed with dil. hydrochloric acid and alcohol.

Cobaltic chloropentamminochloride furnishes violet-red or purple crystals. M. G. Mellon recommended the aq. soln. as a standard colour in colorimetry. The crystals are rhombic bipyramids, having, according to H. Töpsöe, and F. M. Jäger, the axial ratios  $a : b : c = 0.9825 : 1 : 1.5347$ . J. D. Dana wrongly described the crystals as tetragonal; he gave 1.802 for the sp. gr. at  $23^{\circ}$ ; F. M. Jäger gave 1.836 at  $10^{\circ}$ ; the mol. vol. 136.05, and the topic axial ratios  $\chi : \psi : \omega = 4.4067 : 4.4852 : 6.8834$ ; S. M. Jørgensen, 1.802 to 1.808 at  $25^{\circ}/4^{\circ}$ ; F. Ephraim and O. Schütz, 1.783 at  $25^{\circ}$ , and mol. vol. 140.5; and E. Birk, 1.787 at  $25^{\circ}/4^{\circ}$ , and mol. vol. 140.2. R. Klement discussed these results. R. Lorenz and I. Posen calculated 1.7696 for the sp. gr. in vacuo, and 142.7 for the mol. vol. at absolute zero. G. L. Clark and co-workers calculated 16.29 for the mol. vol. of each  $\text{NH}_3$ -group in the complex. Z. H. Skraup and co-workers studied the capillary rise of aq. soln.; and E. N. Gapon, the diffusion. A. B. Lamb and J. W. Marden found that the salt is very stable, and suffered no change when kept for a year. J. S. Böhm and A. Dorabalska observed a heat effect with the salt. F. Rose represented the thermal decomposition of the salt by the equation:  $6[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2 = 6\text{CoCl}_2 + 6\text{NH}_4\text{Cl} + 22\text{NH}_3 + \text{N}_2$ , and the reaction has been utilized in the preparation of cobaltous chloride of a high degree of purity—G. P. Baxter and F. B. Coffin, W. Biltz, O. Ruff and E. Ascher, E. Ascher, etc. S. M. Jørgensen found that the salt in aq. soln. passes into the aquopentamminochloride, and in feebly acidic soln.; R. Pers observed a state of equilibrium,  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons [\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$ ; and H. Freundlich and H. Pape, and E. A. Moelwyn-Hughes showed that the reaction is unimolecular. In a boiling soln., for equilibrium, the soln. contains 42 per cent. of the chloropentammine, and 58 per cent. of the aquopentammine, and A. B. Lamb and J. W. Marden observed that at  $70^{\circ}$ , in soln. with 0.005 to 0.05 mol of salt per litre, and 0.01 to 0.16N-HCl, there is present 61 to 78 per cent. of the aquopentammine; the hydration progresses slowly at  $25^{\circ}$ , and the reaction is unimolecular; with soln. having 0.004 mol per litre, the velocity constant,  $k$ , is 0.046. The subject was studied by A. Benrath, J. N. Brønsted and R. Livingston, K. Matsuno, and H. Freundlich and co-workers. N. R. Dhar observed that  $\text{OH}'$ -ions accelerate the hydration process; and O. W. Gibbs and F. A. Genth, that acids retard the reaction. A. B. Lamb and J. P. Simmons calculated the heat of the reaction to be 2.14 Cals. at  $25^{\circ}$ ; and the mol. heat of soln. of the salt in water as -12.42 Cals. at  $25^{\circ}$ . W. D. Harkins calculated for soln. with 0.002, 0.005, and 0.10 gram-equivalents, per litre, the mol. lowering of the f.p., 5.44, 5.357, and 5.178, respectively; for the factor  $i$  or  $n-1$ , 15, 10—2.93, 2.883, and 2.787, respectively; and for the percentage ionization, 95.6, 92.8, and 89.3, respectively. The absorption spectrum was studied by J. Angerstein, R. Samuel and co-workers, M. Chatelet-Lavollay, R. Lorenz, A. N. Nikolopoulos, Y. Shibata, and E. Valla; the X-ray spectrum, by O. Stelling, and S. Aoyama and

co-workers, and the Raman effect, by D. M. Bose and S. Datta. A. Werner and A. Molati found the mol. conductivity of soln. at 25°, and R. Lorenz and I. Posen, and I. Posen, the eq. conductivity, at 18°. W. D. Harkins and co-workers gave for the eq. conductivity,  $\lambda$ , of soln. with  $C$  gram-equivalents per litre :

$C$	0-0178	0-008384	0-003728	0-0008891	0-0003021
$\lambda$ { 0°	65-00	69-15	72-8	75-25	77-0
25°	120-7	130-2	126-8	142-8	144-7

R. Lorenz and I. Posen gave at the limit  $\lambda_{\infty}=124.1$  at 18°. For the percentage ionization of soln. with 0-002, 0-005, and 0-010, gram-equivalent per litre, the percentage ionization, respectively, 96-0, 94-2, and 89-4, *vide supra*, f.p. data. A. B. Lamb and J. W. Marden—*vide supra*—calculated the degree of hydrolysis from conductivity data. R. Pers studied the dynamics of the hydrolysis:  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons [\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$ . According to R. Schwarz and K. Tede, the hydrolysis:  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2 + 3\text{H}_2\text{O} = \text{Co}(\text{OH})_3 + 3\text{NH}_4\text{Cl} + 2\text{NH}_3$ , proceeds in darkness with an immeasurably slow rate, but in light it proceeds at a speed corresponding with a reaction of the first order. After 60 minutes' exposure to ultra-violet light, a 0-001M-soln., at 25°, had suffered a 3-5 per cent. decomposition, and the velocity constant was  $k=0.0469$ . G. Berger studied the catalytic effect of neutral salts on the photochemical reaction. R. Lorenz found that the transport number of the anion for  $v=80$ , is 0-547 at 17-4°, and 0-549 at 20°; and E. N. Gapon studied the subject. N. R. Dhar and G. Urbain measured the polarization tension, and H. Freundlich and G. Ettisch, the electrokinetic potential—*vide the hexamminochloride*. E. Feytis found that the magnetic susceptibility of the solid is  $-0.295 \times 10^{-6}$  mass unit; S. Berkman and H. Zocher,  $-0.53 \times 10^{-6}$  mass unit; and E. Rosenbohm,  $-0.298 \times 10^{-6}$  mass unit. The magnetic properties were also studied by W. Biltz, L. C. Jackson, D. M. Bose, and H. Moehle.

F. Claudet, and S. M. Jörgensen noted the solubility of the salt in water, and A. Werner observed that 100 grms. of water, at 11-5°, dissolve 0-4 gm. of the chloropentammine; and N. S. Kurnakoff said that 0-232 gm. is dissolved at 0°, and 1-031 grms. at 46-6°. A. B. Lamb and J. P. Simmons found that a litre of water at 0°, 29-7°, and 50°, dissolves, respectively, 2-244, 6-047, and 10-01 grms. F. Ephraim found that a sat. soln. has 0-0170 mol per litre at 19°; and J. N. Brönsted and A. Petersen, 0-00914 mol at 0°, and 0-018 mol at 20°. A. R. Klein studied the action of water, acids, and alkali-lye; and J. N. Brönsted and co-workers, the effect of potassium hydroxide, on various salts on the solubility in aq. and in methanol soln.; and A. Benrath, the effect of hydrochloric acid, potassium iodide, and mercuric chloride. O. W. Gibbs and F. A. Genth found that the salt is decomposed when boiled for a long time with water. O. Ruff and E. Ascher noted that the salt is decomposed by hydrogen chloride. A. Benrath found that at 25°, the following proportions of hydrochloric acid dissolve cobalt in the form of the chloropentamminochloride per 100 grms. of water :

HCl	0-00	0-20	0-60	1-00	2-00	4-00	10-00	30-00 per cent.
Co	0-1337	0-0599	0-0270	0-0200	0-0147	0-0065	0-0040	0-0029

and there is no sign of the formation of a double salt with hydrogen chloride. A. Benrath and H. Pitzler studied the reaction with hydrobromic acid:  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2 + 2\text{HBr} \rightleftharpoons [\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Br}_2 + 2\text{HCl}$ . F. Ephraim observed that the salt is decomposed by sulphuric acid with the evolution of hydrogen chloride, and that ammonia is not taken up by the chloropentammine at -21°. G. T. Morgan and J. D. M. Smith observed that aq. ammonia in an autoclave, at 120°, converts the chloropentammine into the hexammine; and A. Benrath and K. Mienes found the reaction proceeds very slowly, and begins at about 150°. O. W. Gibbs and F. A. Genth noted that nitrous acid converts the chloropentammine into nitropentammine. H. Freundlich and H. Schucht, and K. Matsuno studied the flocculating action on the hydrosol of arsenic sulphide. F. Ephraim observed that

precipitates are produced by the substituted benzene and naphthalene sulphonic acids. As indicated above, the effect of potassium hydroxide on the solubility of the chloropentammine was studied by J. N. Brönsted and co-workers; and the formation of hydrated cobaltic oxide by the alkali-lye was observed by G. F. Hüttig and R. Kassler. According to O. W. Gibbs and F. A. Genth, and S. M. Jörgensen, coloured, crystalline precipitates are produced by potassium ferrocyanide, ferri-cyanide, cobalticyanide, chromate, and dichromate, by ammonium oxalate, molybdate and picrate; by sodium pyrophosphate hydrochloroplatinic acid, mercuric chloride, and stannic chloride. Silver nitrate precipitates only two of the three atoms of contained chlorine, and the subject was studied by O. W. Gibbs and F. A. Genth, R. Lorenz, and P. Job. F. Krauss found that potassium ruthenocyanide gives a crystalline precipitate.

A. Benrath found no sign of the formation of a double salt with potassium chloride when the chloropentamminochloride dissolves in soln. of the alkali chloride, at 25°, when concentrations are expressed in grams per 100 grms. of water :

KCl	.	.	0.00	0.089	0.850	1.093	4.338	6.751	34.460
Co	.	.	0.1337	0.1076	0.0362	0.0161	0.0083	0.0057	0.0007

F. Ephraim and P. Mosimann were unable to prepare double salts of cobaltic chloropentamminochloride with the chlorides of copper, calcium, barium, zinc, cadmium, aluminium, manganese, iron (ic), cobalt, or nickel. O. W. Gibbs reported that a chloroaurate, **gold cobaltic chloropentamminopentachloride**,  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}(\text{AuCl}_4)$ , is formed in dark ruby-red, prismatic crystals by adding auric chloride to a hot, aq. soln. of the chloropentammine. F. Claudet, O. W. Gibbs, and E. Carstanjen reported that with mercuric chloride or sodium mercuric chloride, an aq. soln. of the chloropentamminochloride furnishes **mercuric cobaltic chloropentamminooctochloride**,  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2 \cdot 3\text{HgCl}_2$ , in small, red needles or prisms. A. Benrath observed the formation of this salt in soln. The solubility of the chloropentammine chloride in soln. containing mercuric chloride—when the concentrations are expressed in grms. per 100 grms. of water, at 25°—was :

HgCl <sub>2</sub>	.	0.00	0.1265	0.1680	0.1818	0.228	0.261	0.643	2.33
Co	.	0.1350	0.1525	0.1545	0.1174	0.1148	0.681	0.0514	0.0099

F. Ephraim and P. Mosimann said that the addition of potassium chloride to a soln. of the salt converts it into **mercuric cobaltic chloropentamminotetrachloride**,  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2 \cdot \text{HgCl}_2$ . G. Vortmann and E. Morgulis reported that a double salt is formed with mercuric chloride; and O. W. Gibbs described a salt with  $2\text{HgCl}_2$ , but S. M. Jörgensen could not confirm this. S. M. Jörgensen observed that the salt  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2 \cdot 3\text{HgCl}_2$  is sparingly soluble in cold water, but more soluble in hot water, and it is decomposed into its two components by hydrochloric acid. F. Ephraim said that the sp. gr. of the salt is 3.661 at 25°, and the mol. vol., 290.9. A. Benrath studied the conductivity of aq. soln., and N. R. Dhar found that the mol. conductivity,  $\mu$ , of soln. of a mol of the salt in  $v$  litres, at 30°, is :

$v$	.	.	.	769.4	1538.8	30,776.6	6155.2	12,310.4
$\mu$	.	.	.	265.42	356.34	405.46	445.75	461.88

A. Hiendlmayr prepared **cobaltic fluopentamminochloride**,  $[\text{Co}(\text{NH}_3)_5\text{F}]\text{Cl}_2$ , by the action of hydrochloric acid on a soln. of the corresponding fluoride. It is a dark red powder, soluble in water. Boiling water converts it into  $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{Cl}_3$ . R. Duval prepared **cobaltic formatopentamminochloride**,  $[\text{Co}(\text{NH}_3)_5(\text{COOH})]\text{Cl}_2$ ; and **cobaltic chloropentamminodithionate**,  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{S}_2\text{O}_6$ .

A. Werner,<sup>6</sup> and A. Werner and V. L. King described the preparation and properties of **cobaltic chlorobisethylenediamineamminochloride**,  $[\text{Co}(\text{NH}_3)_2\text{en}_2\text{Cl}]\text{Cl}_2$ ; and S. M. Jörgensen, of the *dihydrate*. J. Petersen studied the lowering of the f.p. of aq. soln.; A. Gordienko, and J. Angerstein, the absorption spectrum; A. Werner and C. Herty, and J. Petersen, the electrical conductivity of aq. soln.; E. Rosenbohm, L. C. Jackson, and L. A. Welo, the magnetic properties; and A. Werner, and S. M. Jörgensen, the chemical properties. The magnetic properties of an optically-active form, the *lævo*-salt, were studied by S. Rosenbohm, and L. C. Jackson. H. E. Watts prepared **cobaltic chlorobispropylenediamineamminochloride**,  $[\text{Co}(\text{NH}_3)_2\text{pn}_2\text{Cl}]\text{Cl}_2$ ; and E. Berl, **cobaltic chlorobisethylenediaminehydroxylaminechloride**,  $[\text{Co}(\text{NH}_2\text{OH})_2\text{en}_2\text{Cl}]\text{Cl}_2$ , as well as double salts with gold and platinum chlorides. A. Werner also reported **cobaltic cis-chlorobisethylenediamineamminochloride**; R. Vogel, and R. Plischke prepared **cobaltic chloropyridinebisethylenediaminechloride**,

[Co en<sub>2</sub>pyCl]Cl<sub>2</sub>, as well as the double salts, zinc cobaltic chloropyridinebisethylenediaminechloride, [Co en<sub>2</sub>pyCl]Cl<sub>2</sub>.ZnCl<sub>2</sub>.H<sub>2</sub>O; mercuric cobaltic chloropyridinebisethylenediaminechloride, [Co en<sub>2</sub>pyCl]Cl<sub>2</sub>.HgCl<sub>2</sub>.H<sub>2</sub>O; stannous cobaltic chloropyridinebisethylenediaminechloride, [Co en<sub>2</sub>pyCl]Cl<sub>2</sub>.SnCl<sub>2</sub>; and also ferric cobaltic chloropyridinebisethylenediaminechloride; J. Meisenheimer and E. Kiderlen, cobaltic chloroethylaminebisdiethylenediaminechloride, [Co en<sub>2</sub>(C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub>)Cl]Cl<sub>2</sub>; the *cis*- and *trans*-forms of cobaltic chloroallylaminebisethylenediaminechloride, [Co en<sub>2</sub>C<sub>3</sub>H<sub>5</sub>.NH<sub>2</sub>)Cl]Cl<sub>2</sub>; cobaltic chloroanilinebisethylenediaminechloride, [Co en<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>.NH<sub>2</sub>)Cl]<sub>2</sub>; cobaltic chloro-*p*-toluidinebisethylenediaminechloride, [Co en<sub>2</sub>(C<sub>7</sub>H<sub>7</sub>.NH<sub>2</sub>)Cl]<sub>2</sub>; and cobaltic chlorobenzylaminebisethylenediaminechloride, [Co en<sub>2</sub>(C<sub>7</sub>H<sub>7</sub>.NH<sub>2</sub>)Cl]Cl<sub>2</sub>.

A. Werner<sup>7</sup> obtained **cobaltic cis-chloroaquotetramminochloride**, [Co(NH<sub>3</sub>)<sub>4</sub>-(H<sub>2</sub>O)Cl]Cl<sub>2</sub>, by keeping the diaquotetramminochloride for a long time, and by the hydration of trans-dichlorotetramminochloride; W. Schramm, by the action of malonic acid on the diaquotetramminochloride, or on hydroxyaquotetramminochloride; S. M. Jörgensen, and G. Vortmann and co-workers, by treating the carbonatotetramminochloride with cold, 1:1-hydrochloric acid, and then with the conc. acid; and S. M. Jörgensen, by the action of ice-cold hydrochloric acid on chloroaquotetramminosulphate. The violet powder was found by F. M. Jäger to have rhombic bipyramidal crystals with axial ratios  $a:b:c=0.908:1:0.925$ , and sp. gr. 1.847 at 20°; the mol. vol., 136.05; and topic axial ratios  $\chi:\psi:\omega=4.4067:4.4852:6.8834$ . J. D. Dana gave 1.802 for the sp. gr.; E. Birk, and W. Biltz, 1.825 at 25°/4°, and mol. vol. 137.8. H. Skraup and co-workers studied the capillary rise of the aq. soln.; J. Petersen, the lowering of the f.p. of aq. soln.; J. Angerstein, A. Gordienko, Y. Shibata, A. N. Nikolopulos, R. Luther and A. N. Nikolopulos, and K. Matsuno, the absorption spectrum; and J. Petersen, the electrical conductivity of aq. soln. A. Werner and A. Miolati found the mol. conductivity,  $\mu$ , of soln. with a mol of the salt in  $v$  litres, at 25°, to be:

$v$	128	256	512	1024
$\mu$ { at the start	221.3	253.7	293.7	318.9
in 5 hrs.	321.3	342.5	363.2	380.6

The maximum attained in 5 hrs. shows that the transformation to the diaquotetramminochloride is complete. J. N. Brönsted studied the rate of the transformation: [Co(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)Cl]<sup>+</sup>+H<sub>2</sub>O=[Co(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>+</sup>+Cl<sup>-</sup>, which is a reaction of the first order at 20°. S. M. Jörgensen observed that at ordinary temp. a gram of the chloroaquotetramminochloride dissolves in about 40 grms. of water; and J. N. Brönsted and A. Petersen, that a sat. soln. at 0° contains 0.057 mol per litre, and at 20°, 0.11 mol. A. Benrath and K. Andreas observed no change in the nature of the solid phase when hydrochloric acid is added to the aq. soln. at 25°, but the solubility of the salt drops from about 1 per cent. of Co in soln. to 0.01 per cent. Co when 28.93 per cent. HCl is present. S. M. Jörgensen observed that the cold, sat. soln. when freshly prepared, gives crystalline precipitates with conc. hydrochloric, dil. nitric or hydrofluosilicic acid, with ammonium sulphate or oxalate, with sodium hydrophosphate, with potassium chromate, hydrochloroplatinic acid, and mercuric chloride, but not with sodium dithionate, or potassium chloroplatinite. W. Schramm observed that oxalic acid forms [Co(NH<sub>3</sub>)<sub>4</sub>(C<sub>2</sub>O<sub>4</sub>)]Cl, but malonic acid has very little action. P. Job, and S. M. Jörgensen observed that with freshly-prepared soln., silver nitrate precipitates only two-thirds of the contained chlorine, but all is precipitated with aged soln. where the chloraquotetrammine has passed into diaquotetrammine. Sodium nitrite converts the chloroaquotetrammine into the cis-nitro-salt. K. Matsuno studied the flocculation of the hydrosol of arsenic sulphide by this salt. G. Vortmann and co-workers prepared **cobaltic chloroaquotetramminooctochloride**, [Co(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)Cl]Cl<sub>2</sub>.3HgCl<sub>2</sub>, in small, violet prisms, sparingly soluble in cold water, freely soluble in hot water.

A. Werner prepared **cobaltic chloroaquobisethylenediaminechloride**, [Co en<sub>2</sub>(H<sub>2</sub>O)Cl]Cl<sub>2</sub>, by hydrating dichlorobisethylenediaminechloride, or, according to W. Schramm, by the

action of malonic acid on that salt; and it is also produced by the action of conc. hydrochloric acid on the corresponding sulphate. The salt was found by A. Werner to be fairly stable in cold, aq. soln., but when heated it produces a complicated mixture of products studied by A. Uspensky and K. Tschibisoff. The absorption spectrum was investigated by C. Schleicher, and A. Uspensky and K. Tschibisoff. J. Meisenheimer and E. Kiderlen studied the reaction with aniline; and F. M. Jäger and P. Koets, the reaction with triaminotriethylamine. H. Fischlin separated the *dextro-salt* and the *laevo-salt* by treating the optically-active bromide of the series with hydrochloric acid. The reddish-black, cubic crystals are freely soluble in water. The sp. rotation of a 0.1 per cent. aq. soln. is  $252^\circ$  for Na-light.

A. Werner prepared **cobaltic chlorodiaquotriamminochloride**,  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_2\text{Cl}]\text{Cl}_2$ , by the action of conc. hydrochloric acid on the violet sulphate. E. Birk found the sp. gr. of the dark violet, crystalline powder to be 1.872 at  $25^\circ/4^\circ$ , and the mol. vol. 134.9. W. Biltz also studied the contraction which occurs during the formation of the salt.

Basic cobaltic pentammines were studied by O. W. Gibbs and F. A. Genth,<sup>8</sup> H. Schiff, S. M. Jörgensen, and A. Werner. H. Schiff, and C. D. Braun obtained **cobaltic hydroxypentamminochloride**,  $[\text{Co}(\text{NH}_3)_5(\text{OH})]\text{Cl}_2 \cdot \text{H}_2\text{O}$ , by treating either the hydroxypentamminosulphate, or aquopentamminochloride, with barium chloride in a feebly ammoniacal soln. P. Job studied its formation from the aquopentammine. A. Werner obtained it by the action of ammonia on the aquopentamminochloride; and G. T. Morgan and J. D. M. Smith, by mixing an ice-cold soln. of 23.8 grms. of hexahydrated cobalt chloride in 15 c.c. of water with 8.5 c.c. of  $12\text{N}\text{-H}_2\text{O}_2$ , and then with 57 c.c.  $18\text{N}\text{-NH}_4\text{OH}$ , added slowly. The evaporation of the liquor furnishes the chloride in purple-red needles; A. Werner obtained the salt in violet-red scales. M. Chatelet-Lavollay, and Y. Shibata and G. Urbain studied the absorption spectrum; and N. R. Dhar and G. Urbain, the polarization tension—*vide supra*, the hexammine. According to A. Werner, the salt forms a bluish-red solution in water; it liberates ammonia from ammonium salts; and according to H. Schiff, warm hydrochloric acid converts it into chloropentamminochloride. J. N. Brönsted studied the catalysis of acids and bases by the salt; and J. N. Brönsted and E. A. Guggenheim, the effect on the mutarotation of glucose.

A. Werner prepared **cobaltic hydroxyaquotetramminochloride**,  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{OH})]\text{Cl}_2$ , by the action of cold, conc., aq. ammonia on the diaquotetramminochloride; and J. V. Dubsy, what he regarded as a *monohydrate*, by the action of aq. ammonia on octamminodiolchloride. The violet-red salt liberates ammonia from ammonium salts; it does not form silver oxide with silver nitrate, showing that the OH-group is part of the inner complex. The compound is not acetylated by the action of acetic anhydride, but it is converted into octamminodiolchloride, and the same transformation occurs when the salt is heated to  $100^\circ$ . The salt is unstable in aq. soln. W. Schramm found that oxalic acid converts it into the oxalatotetrammine, and malonic acid forms the chloroaquo-salt.

M. Rosner prepared **cobaltic hydroxydipyridinetriamminochloride**,  $[\text{Co}(\text{NH}_3)_3\text{py}_2(\text{OH})]\text{Cl}_2 \cdot 5\text{H}_2\text{O}$ ; and A. Werner obtained **cobaltic cis-hydroxyaquobisethylenediaminechloride**,  $[\text{Co}(\text{en})_2(\text{H}_2\text{O})(\text{OH})]\text{Cl}_2 \cdot \text{H}_2\text{O}$ , by the action of a soln. of pyridine on cis-diaquobisethylenediaminechloride; and J. Meisenheimer and E. Kiderlen, and A. Werner, **cobaltic trans-hydroxyaquobisethylenediaminechloride**, by the action of an aq. soln. of an organic base on trans-diaquobisethylenediaminechloride. A. Werner also obtained it by warming cis-dichlorobisethylenediaminechloride with conc. aq. ammonia. A. Werner prepared **cobaltic hydroxyaquodipyridinediamminochloride**,  $[\text{Co}(\text{NH}_3)_2\text{py}_2(\text{H}_2\text{O})(\text{OH})]\text{Cl}_2$ , by treating dichloroaquodipyridinediamminochloride with pyridine and potassium chloride in cold, aq. soln. The salt was also studied by J. Meyer and co-workers. Y. Nakasuka and H. Inuma studied the **cobaltic bisdimethylglyoximediamines**.

#### *The $\text{CoA}_4$ or Tetrammine Family.*

E. Böhm<sup>9</sup> obtained **cobaltic difluotetramminochloride**,  $[\text{Co}(\text{NH}_3)_4\text{F}_2]\text{Cl}$ , by treating a soln. of carbonatotetramminochloride, in as little water as possible,

with conc. hydrofluoric acid, until the evolution of carbon dioxide had ceased. On standing for some days at room temp., the soln. deposits dark red crystals, fairly stable in air, freely soluble in water. H. Siebt also prepared **cobaltic trans-difluorobisethylenediaminechloride**,  $[\text{Co en}_2\text{F}_2]\text{Cl}$ , in pale green needles, by treating an ice-cold soln. of the fluoride of the series with ammonium chloride.

A series of cobaltic dichlorotetrammines has been prepared by O. W. Gibbs and F. A. Genth,<sup>10</sup> F. Rose, G. Vortmann, R. Pers, S. M. Jörgensen, and A. Werner and co-workers. A. Werner and A. Klein prepared **cobaltic trans-dichlorotetramminofluoride**, presumably  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{F}$ , by treating a conc. soln. of the corresponding sulphate with ammonium or potassium fluoride. Dichroic crystals are precipitated, and they are freely soluble in water.

A. Werner obtained **cobaltic dichlorotetramminochloride**,  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl} \cdot \frac{1}{2}\text{H}_2\text{O}$ , by shaking carbonatotetramminochloride at ordinary temp. with twice as much absolute alcohol saturated with hydrogen chloride at  $0^\circ$ , until the evolution of carbon dioxide ceases. The product is washed with absolute alcohol until free from acid; it is also obtained by triturating octamminodiolchloride with saturated hydrochloric acid, and then washing the product with alcohol. W. Schramm prepared the salt, and A. Werner made a product of a high degree of purity as follows:

Two grams of the dithionate of the series were triturated with 4 grms. of ammonium chloride and 4 c.c. of water; the dark blue product was then rubbed up with an excess of ammonium chloride and a little water, dissolved in as little cold water as possible, and ammonium chloride added to the soln. for precipitation. The product was washed with water, and then with alcohol and ether.

The violet prisms and needles lose their water at  $60^\circ$ . The salt is freely soluble in water, forming a blue soln. which rapidly becomes violet or reddish-violet as the dichlorotetrammine passes into the aquo-salt. A. N. Nikolopulos, and R. Luther and A. N. Nikolopulos studied the absorption spectrum of the soln. K. Andréas studied the systems:  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}-\text{HCl}-\text{H}_2\text{O}$ , at  $25^\circ$ , and also  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}-\text{NH}_3-\text{H}_2\text{O}$ , at  $25^\circ$ . A. Werner noted that a freshly-prepared aq. soln. precipitates the corresponding salt of the series when treated with dil. sulphuric acid, conc. nitric acid, ammonium bromide, sulphate, nitrate, or thiocyanate, or sodium dithionate; potassium chloroplatinite gives a bluish-violet precipitate, that with hydrochloroplatinic acid is greyish-green, and that with potassium dichromate, bronze, and potassium chromate, greyish-brown. No precipitation occurs with sodium nitrite, potassium chlorate or cyanide, or with ammonium oxalate.

O. W. Gibbs and F. A. Genth, F. Rose, and G. Vortmann obtained the corresponding **cobaltic trans-dichlorotetramminochloride**,  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl} \cdot \text{H}_2\text{O}$ ; and S. M. Jörgensen recommended preparing it by mixing 10 grms. of powdered chloro-aquotetramminochloride (or diaquotetramminosulphate) with 50 c.c. of conc. sulphuric acid, and after some hours, adding to the ice-cold liquid, 50 c.c. of conc. hydrochloric acid. After the mixture has stood some hours, it begins to crystallize. In two days, the crystals are washed with dil. sulphuric acid, then with dil. hydrochloric acid until free from sulphuric acid, and then with alcohol until free from acid. A. Uspensky and K. Tschibisoff studied the stereoisomerides of the tetrammines. The green crystals of the monohydrate were found by F. Ephraim and O. Schütz to have a sp. gr. of 1.844 at  $25^\circ$ , and a mol. vol. of 136.5, and the anhydrous salt a sp. gr. of 1.799 at  $25^\circ$ , and a mol. vol. of 129.8. E. Birk gave 1.860 for the sp. gr. of the anhydrous salt, and 125.5 for the mol. vol. H. Skraup and co-workers measured the capillary rise of the aq. soln. E. Petersen measured the lowering of the f.p. of aq. soln. A. N. Nikolopulos, and R. Luther and A. N. Nikolopulos, the absorption spectrum; and O. Stelling, and S. Aoyama and co-workers, the X-ray spectrum. E. Petersen found the mol. conductivity,  $\mu$ , of a soln. with a mol of the salt in  $v$  litres, to be:

$v$	.	.	25	50	100	200	1600	3200
$\mu$ { $0^\circ$ .	.	.	94.0	106.0	115.1	128.1	143.2	156.1
$\mu$ { $25^\circ$ .	.	.	—	193.1	245.7	287.4	376.8	391.8

The values increase with time, owing to the hydrolysis of the salt. The data were discussed by A. Werner and C. Herty, and W. D. Harkins and co-workers. The aquation of the salt in aq. soln.:  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl} \rightarrow [\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2 \rightarrow [\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{Cl}_3$ , was found by K. Matsuno to be a unimolecular reaction. The first reaction occupies 30 minutes under conditions where the second one occupies 24 hrs. R. Schwarz and K. Tede studied the photolysis of the soln. in ultra-violet light. N. R. Dhar and G. Urbain studied the polarization tension. E. Rosenbohm gave  $-2.24 \times 10^{-6}$  mass unit for the magnetic susceptibility of the salt; and the magnetic properties were studied by E. Feytis, W. Biltz, and L. C. Jackson. J. N. Brönsted and A. Petersen found that the sat. aq. soln. at  $0^\circ$  contains 0.0141 mol per litre; and A. Werner and P. Larisch, 0.366 gm. per 100 grms. of water at  $0^\circ$ . The solid phase in hydrochloric acid is not stable at  $25^\circ$ , but forms the chloroaquatetramminochloride; the solubility of the salt falls from 0.98 per cent. Co to 0.01 per cent. Co in the presence of 29.07 per cent. HCl. Silver nitrate was found by A. Werner to give a precipitate with the aq. soln., probably a double salt. A. Werner and A. Klein found that with auric chloride, green crystals of **gold cobaltic dichlorotetramminotetrachloride**,  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{AuCl}_4$ , are formed; and with a mercuric chloride, a green crystalline precipitate of **mercuric cobaltic dichlorotetramminotetrachloride**,  $2[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl} \cdot \text{HgCl}_2$ , was prepared by A. Werner and A. Klein, and G. Vortmann. The latter also obtained **mercuric cobaltic dichlorotetramminotrichloride**,  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl} \cdot \text{HgCl}_2$ . E. Böhm prepared **cobaltic difluorotetramminochloride**,  $[\text{Co}(\text{NH}_3)_4\text{F}_2]\text{Cl}$ , by dissolving carbonatotetramminochloride in the smallest possible quantity of water, and treating the soln. with hydrofluoric acid until the evolution of carbon dioxide ceases. Dark red crystals separate from the liquid in a few days when kept at room temp. The crystals are fairly stable in air, and freely soluble in water. H. Seibt also prepared **cobaltic trans-difluorobisethylene-diaminochloride**,  $[\text{Co en}_2\text{F}_2]\text{Cl}$ , by the action of ammonium chloride on a cold soln. of the fluoride.

A. Werner and R. Feenstra,<sup>11</sup> and T. S. Price prepared **cobaltic trans-dichlorotetrapyridinechloride**,  $[\text{Co py}_4\text{Cl}_2]\text{Cl} \cdot 6\text{H}_2\text{O}$ , in green plates found by R. Lorenz and I. Posen, and I. Posen to have a sp. gr. of 1.3990; the salt dehydrated at  $61^\circ$  has a sp. gr. 1.461. The eq. conductivity, and the transport number of the anion were measured by R. Lorenz and I. Posen, and the chemical properties were studied by A. Werner and R. Feenstra, and T. S. Price. A. Werner and R. Feenstra reported **gold cobaltic dichlorotetrapyridinetetrachloride**,  $[\text{Co py}_4\text{Cl}_2](\text{AuCl}_4)$ ; and T. S. Price, **mercuric cobaltic dichlorotetrapyridinedodecachloride**,  $2[\text{Co py}_4\text{Cl}_2]\text{Cl} \cdot 3\text{HgCl}_2$ .

A. Werner, R. Plischke, R. Vogel, A. Uspensky and K. Tschibisoff, and S. M. Jörgensen obtained **cobaltic cis-dichlorobisethylenediaminechloride**,  $[\text{Co en}_2\text{Cl}_2]\text{Cl} \cdot \text{H}_2\text{O}$ , in dark violet crystals requiring about 25 grms. of water to dissolve a gram of salt. The constitution of the salts of this series was discussed by A. Werner, S. M. Jörgensen, J. A. N. Friend, and E. E. Turner. K. Andreas studied the action of hydrochloric acid, and of aq. ammonia on the salt. J. Petersen studied the lowering of the f.p. of water; A. Uspensky and co-workers, J. Lifschitz and E. Rosenbohm, R. Samuel, M. L. Ernsberger and W. R. Brode, W. Kuhn and K. Bein, and C. Schleicher, the absorption spectrum; O. Stelling, the X-ray spectrum; A. Werner and C. Herty, L. Tschugaeff, W. D. Harkins and co-workers, and J. Petersen, the electrical conductivity; E. Rosenbohm, L. C. Jackson, and W. Biltz, the mechanical properties; and S. M. Jörgensen, A. Werner and co-workers, T. S. Price and S. A. Brazier, A. Uspensky and K. Tschibisoff, K. Matsuno, and J. Meisenheimer and K. Kiderlen, the chemical properties. A. Werner and co-workers prepared optically-active forms, where the sp. rotation of a 0.25 per cent. aq. soln. of the *dextro*-salt was  $184^\circ$ , and of the *laevo*-salt,  $-200^\circ$ . S. M. Jörgensen prepared violet scales of **mercuric cobaltic dichlorobisethylenediaminetrichloride**,  $[\text{Co en}_2\text{Cl}_2]\text{Cl} \cdot \text{HgCl}_2$ . S. M. Jörgensen, H. Schwarz, H. Siebt, E. Schmidt, K. R. Lange, W. A. Redeker, and A. Werner prepared **cobaltic trans-dichlorobisethylenediaminechloride**,  $[\text{Co en}_2\text{Cl}_2]\text{Cl}$ , in emerald green, prismatic crystals. A. Werner and C. Herty, and J. Petersen measured the lowering of the f.p. in aq. soln.; C. Schleicher, A. Gordienko, Y. Shibata, Y. Shibata and G. Urbain, A. Uspensky and K. Tschibisoff, M. L. Ernsberger and W. R. Brode, and J. Lifschitz and E. Rosenbohm, the absorption spectrum; A. Werner and C. Herty, and L. Tschugaeff, the electrical conductivity; and S. Berkman and H. Zocher, the magnetic susceptibility. The aquation of the salt in aq. soln.:  $[\text{Co en}_2\text{Cl}_2]\text{Cl} \rightarrow [\text{Co en}_2(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2 \rightarrow [\text{Co en}_2(\text{H}_2\text{O})_2]\text{Cl}_3$ , was studied by A. Uspensky and K. Tschibisoff.



bisoff, Y. Shibata, A. Werner, S. M. Jörgensen, K. Matsuno, and A. Benrath and K. Andreas. The chemical properties were studied by A. Werner and co-workers, S. M. Jörgensen, J. Meisenheimer and E. Kiderlen, and W. Schramm. T. S. Price and S. A. Brazier noted the formation of addition products with lactic acid, and malonic acid. S. M. Jörgensen, A. Werner and co-workers, P. Pfeiffer and co-workers prepared **cobaltic trans-dichlorobisethylenediaminehydrochloride**,  $[\text{Co en}_2\text{Cl}_2]\text{Cl} \cdot \text{HCl} \cdot 2\text{H}_2\text{O}$ , and the properties of the compound were studied by A. Werner, S. M. Jörgensen, T. S. Price and S. A. Brazier, S. Berkman and H. Zocher, and A. Uspensky and K. Tschibisoff. P. Pfeiffer and M. Tapuach prepared **antimony cobaltic dichlorobisethylenediaminehexachloride**,  $[\text{Co en}_2\text{Cl}_2]\text{SbCl}_6$ ; and S. M. Jörgensen, mercuric cobaltic trans-dichlorobisethylenediamine-trichloride,  $[\text{Co en}_2\text{Cl}_2]\text{Cl} \cdot \text{HgCl}_2$ . G. and P. Spacu prepared copper cobaltic dichlorobisethylenediaminechloride,  $[\text{Co en}_2\text{Cl}_2]_2\text{CuCl}_4$ ; cadmium cobaltic dichlorobisethylenediaminechloride,  $[\text{Co en}_2\text{Cl}_2]_2\text{CdCl}_4$ ; stannous cobaltic dichlorobisethylenediaminechloride,  $[\text{Co en}_2\text{Cl}_2]\text{SnCl}_3$ ; stannic cobaltic dichlorobisethylenediaminechloride,  $[\text{Co en}_2\text{Cl}_2]_2\text{SnCl}_6$ ; bismuth cobaltic dichlorobisethylenediaminechloride,  $[\text{Co en}_2\text{Cl}_2]_3\text{BiCl}_6$ .

H. E. Watts, and A. Werner and A. Fröhlich obtained **cobaltic cis-dichlorobispropylenediaminechloride**,  $[\text{Co pn}_2\text{Cl}_2]\text{Cl}$ , in violet crystals, and **cobaltic trans-dichlorobispropylenediaminechloride**,  $[\text{Co pn}_2\text{Cl}_2]\text{Cl}$ , in pale green plates, and the salt was also examined by A. Werner, and W. Schramm. A. Werner and A. Fröhlich obtained **cobaltic dichlorobispropylenediaminehydrochloride**,  $[\text{Co pn}_2\text{Cl}_2]\text{Cl} \cdot \text{HCl} \cdot 2\text{H}_2\text{O}$ ; and they also prepared **gold cobaltic dichlorobispropylenediaminetetrachloride**,  $[\text{Co pn}_2\text{Cl}_2]\text{AuCl}_4$ ; and mercuric cobaltic dichlorobispropylenediamineheptachloride,  $3[\text{Co pn}_2\text{Cl}_2]\text{Cl} \cdot 2\text{HgCl}_2$ . A. Werner and G. Lindenberg prepared **cobaltic trans-dichlorotrimethylenediaminechloride**,  $[\text{Co}(\text{C}_3\text{H}_{10}\text{N}_2)_2\text{Cl}_2]\text{Cl}$ , in green, prismatic crystals; F. M. Jäger and H. B. Blumendal cobaltic cis-dichlorobiscyclopentanediaminechloride,  $[\text{Co}(\text{C}_5\text{H}_{12}\text{N}_2)_2\text{Cl}_2]\text{Cl}$ , and also cobaltic trans-dichlorobiscyclopentanediaminechloride; A. Werner prepared **cobaltic dichlorobispyridinediaminediaminochloride**,  $[\text{Co}(\text{NH}_3)_2\text{py}_2\text{Cl}_2]\text{Cl}$ , as a green, crystalline powder; A. Werner and F. Chaussey, and C. Rix, **cobaltic trans-dichloroethylenediaminediaminochloride**,  $[\text{Co}(\text{NH}_3)_2\text{enCl}_2]\text{Cl}$ , in green crystals; and C. J. Dippel and F. M. Jäger, **cobaltic dichlorobisdiaminopentanochloride**,  $[\text{Co ptn}_2\text{Cl}_2]\text{Cl}$ , with  $\alpha\beta\delta$ - and  $\beta\beta\delta$ -aminopentane; and E. N. Gapon, **cobaltic dichlorobisphenylethylenediaminochloride**,  $[\text{Co}(\text{CH}_2\text{NH}_2\text{C}_6\text{H}_5)_2\text{Cl}_2]\text{Cl}$ —cis- and trans-forms.

P. Job observed that when alkali hydroxide is added gradually to a soln. of cobaltic diaquotetramminochloride (or sulphate), the measurements of the e.m.f. show that no hydroxyl ions are present until more than 2 eq. of alkali have been added. The soln. contains **cobaltic dihydroxytetramminochloride**:  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{Cl}_3 + 2\text{KOH} = [\text{Co}(\text{NH}_3)_4(\text{OH})_2]\text{Cl} + 2\text{KCl} + 2\text{H}_2\text{O}$ . H. J. S. King found that the electrical conductivity,  $\lambda$ , at  $0^\circ$ , of soln. with a mol of the dihydroxytetrammine, in  $v$  litres, is:

$v$	.	.	33.98	67.96	79.94	159.9	261.4	524.4	1036
$\lambda$	.	.	52.25	55.08	55.71	57.72	59.32	61.16	69.60

The mobility of the ion is 23.0, and  $n=1.50$ .

In 1871, F. Rose<sup>12</sup> reported greyish-green **cobaltic dichloroaquotriamminochloride**,  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})\text{Cl}_2]\text{Cl}$ , to be formed when an ammoniacal soln. of cobaltous chloride is oxidized until cobaltic hydroxide begins to separate, and then mixed with an excess of hydrochloric acid and allowed to crystallize. S. M. Jörgensen observed that the same salt is produced when the acid sulphate of the series is treated with 1:1 hydrochloric acid; and when a soln. of cobaltic trinitratotriammine is treated with dil. hydrochloric acid, allowed to stand 24 hrs., and then treated with conc. acid. J. Meyer and co-workers employed a somewhat similar process for the greyish-green salt. S. M. Jörgensen, and J. N. Brönsted and K. Volquartz said that the compound appears in two forms: (1) By precipitation from the soln. by the addition of some drops of hydrochloric acid to a soln. of the chloride in conc. hydrochloric acid, the salt is obtained in black, stable crystals which are dichroic—pale red and dark green. (2) By adding 2 vols. of conc. hydrochloric acid to 1 vol. of an aq. soln. of the chloride, thin, hexagonal plates are produced, and they are unstable, and not dichroic. A. Werner prepared a grey form of the salt by rubbing up chlorodiaquotriamminosulphate with conc. hydrochloric acid, pressing the product between porous tiles, and washing with alcohol until free from acid. A. Werner said that the two products are not the same; and K. Matsuno guessed that the greyish-green form is the *trans-salt*, and the grey form, the *cis-salt*.

E. Birk gave 1.908 for the sp. gr. of the greyish-green crystals at  $25^{\circ}/4^{\circ}$ , and 122.9 for the mol. vol. S. M. Jörgensen found that the dry salt is slowly decomposed when it is heated. The absorption spectrum was studied by K. Matsuno; and the X-ray spectrum, by O. Stelling. K. Matsuno showed that the salt is partly hydrolyzed in aq. soln.; and A. Werner and co-workers found that the electrical conductivity in aq. soln. rapidly increases. The conductivity of a mol of the salt in 100 litres at  $0^{\circ}$ , changed in 250 seconds from 81.32 to 148.51. S. M. Jörgensen also found that the salt is very unstable in aq. soln., and silver nitrate precipitates all the chlorine from the freshly-prepared soln. Conc. sulphuric acid acts on the solid with the evolution of hydrogen chloride. A soln. of sodium chloroplatinate precipitates  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_3]_2(\text{PtCl}_6)_3 \cdot 4\text{H}_2\text{O}$ . Phosphoric acid precipitates cobaltous phosphate. R. Klement studied this subject. S. M. Jörgensen observed that oxalic acid precipitates indigo-blue chloro-oxalatotriammine. H. Kaneko studied the effect of the salt on the viscosity of aq. soln. of albumin.

A. Werner and A. Grün, W. Tupizina, and A. Werner and F. Chaussy prepared **cobaltic trans-dichloroquoethylenediamineamminochloride**,  $[\text{Co}(\text{NH}_3)_n(\text{H}_2\text{O})\text{Cl}_2]\text{Cl}$ , by rubbing up trinitratoethylenediamineammine with conc. hydrochloric acid whilst the mixture is being heated on a water-bath; dissolving the product in the smallest amount of water possible, and adding hydrochloric acid. The small, greenish-black needles so obtained are feebly dichroic.

A. Werner prepared blue **cobaltic dichlorodiaquodiamminochloride**,  $[\text{Co}(\text{NH}_3)_2(\text{H}_2\text{O})_2\text{Cl}_2]\text{Cl}$ , by triturating chlorotriaquodiamminosulphate with conc. hydrochloric acid, and pressing the product between porous tiles. The green powder is freely soluble in water, forming a blue soln. What is apparently an isomeric form appears in pale green, dichroic needles, which furnish an emerald-green, aq. soln. which in a few seconds becomes indigo-blue, then violet, and finally red. This variety was obtained by A. Werner, A. Werner and R. Feenstra, S. M. Jörgensen, and E. H. Riesenfeld and R. Klement, by treating potassium tetranitrodiamminocobaltate with conc. sulphuric acid, and slowly adding hydrochloric acid; or by treating the ammonium salt with hydrochloric acid and passing hydrogen chloride through the ice-cold liquid. A. Werner obtained it by adding ice-cold, conc. hydrochloric acid slowly to the sulphate of the series. The acidic soln. furnishes the moss-green crystals, and neutral soln., pale green crystals. The aq. soln. is emerald green. The conductivity measurements of A. Werner and A. Miolati show that the salt in soln. passes into the tetraquo-salt. N. R. Dhar and G. Urbain measured the polarization tension—*vide supra*, the hexammine. The salt is decomposed by phosphoric acid, and R. Klement studied the action of phosphates on the salt.

J. Meisenheimer and E. Kiderlen<sup>13</sup> prepared **cobaltic chlorohydroxybisethylenediaminechloride**,  $[\text{Co en}_2(\text{OH})\text{Cl}_2]\text{Cl} \cdot \text{H}_2\text{O}$ , by rubbing up trans-dichlorobisethylenediaminechloride with a soln. of diethylamine in iced-water so that only partial solution occurs. The crystalline mush is drained by suction, washed with 70 per cent. alcohol, and finally with ordinary alcohol and ether. The compound is also obtained by shaking an aq. soln. of the praseoehloride with methylbenzylamine. The dove-grey crystals are freely soluble in water, forming a carmine-red soln., and in dil. hydrochloric acid, forming a green soln. The water is lost at  $80^{\circ}$  in vacuo, and a structural change simultaneously occurs. When the aq. soln. is warmed, it forms the hydroxyaquochloride, which is precipitated by alcohol; and the dissolution of the salt in 15 per cent. hydrochloric acid, and precipitation with alcohol and ether furnishes the greyish-green chloro-aquochloride. The salt was studied by J. C. Bailar and R. W. Auten.

T. S. Price and S. A. Brazier obtained **cobaltic sulphodiacetabisethylenediaminechloride**,  $[\text{Co en}_2(\text{C}_2\text{H}_4\text{O}_2\text{S})]\text{Cl} \cdot \text{H}_2\text{O}$ , in small, rose-red plates; freely soluble in water; and decomposed at  $115^{\circ}$ ; a sienna-brown gold **cobaltic sulphodiacetabisethylenediaminechloride**,  $[\text{Co en}_2(\text{C}_2\text{H}_4\text{O}_2\text{S})]\text{AuCl}_4$ .

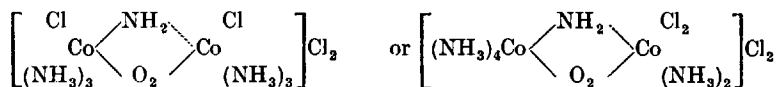
#### *The $\text{CoA}_3$ or Triammine Family.*

A. Werner and E. Bindschedler<sup>14</sup> prepared **cobaltic trichlorotriammine**,  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$ , by rubbing up 10 grms. of hexamminetriolchloride with 30 c.c. of cold, conc. hydrochloric acid, and extracting the violet crystalline mush with cold

water until a bluish-green residue is formed. This was washed with alcohol and ether, and dried over sulphuric acid. E. Birk said that the yield is increased by working, at as low a temp. as possible, with saturated hydrochloric acid. The sp. gr. is 1.932 at 25°/4°, and the mol. vol. is 112.0. O. Stelling studied the X-ray spectrum. A. Werner and E. Bindschedler observed that the salt is sparingly soluble in cold water. The aq. soln. is aquated when allowed to stand a long time, or when heated. Conc. hydrochloric acid forms dichloroaquotriamminochloride; but conc. nitric acid has no action. The constitution was discussed by E. Gapon, J. A. N. Friend, and E. E. Turner.

### The Peroxo-Salts.

F. Rose<sup>15</sup> said that a *schwarze Salz* is produced along with other chlorides when ammoniacal soln. of cobalt salts are oxidized by air for not too long a time, and in the cold, and it is very sparingly soluble in dil. hydrochloric acid. Translating his equivalent formula, his analysis gave him  $\text{Co}_9\text{Cl}_{22}\text{ON}_{32}\text{H}_{90}$  to 92. O. W. Gibbs represented F. Rose's data by the simpler formula:  $\text{Co}_2(\text{NH}_3)_6\text{OCl}_4\cdot\text{NH}_4\text{Cl}$ , but the idea that the product is a complex salt is not in accord with its behaviour. The salt had been previously observed by E. Frémy. G. Vortmann suggested the formula:  $\text{Co}_2(\text{NH}_3)_6\cdot\text{Cl}_4\text{NH}_4\text{Cl}$ , and designated the product **cobaltic melanochloride**, —μελας, black. The products so far prepared were shown by A. Werner to be mixtures of a sparingly soluble, dark grey salt, **cobaltic dichloro-μ-amino-peroxo-hexamminochloride** :



and the sparingly soluble melanochloride which he considered to be **cobaltic trichloroaquo-μ-amino-hexamminochloride** :



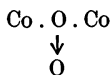
When an amine or  $\text{NH}_2$ -group in a salt is associated with two metal atoms, A. Werner called it a *μ-amino-salt*; when in the salt an imine or  $\text{NH}$ -group is similarly associated, a *μ-imino-salt*; when in the salt an  $\text{OH}$ -group is similarly associated, an *ol-salt*; and when in the salt an  $\text{O}_2$ -group is similarly associated, a *peroxo-salt*—if the  $\text{O}_2$ -group is not so bridged, it is called an *ozo-salt*, just as an unbridged  $\text{OH}$ -group is called a hydroxy-salt. A. Werner recommended preparing cobaltic melanochloride as follows :

A mixture of 650 grms. of cobalt chloride with 400 c.c. of water and 2 litres of 25 per cent. ammonia is heated to boiling, filtered from the precipitated cobalt oxide, and exposed to the air for 48 hours. The resulting brownish-red solution is filtered from the crystals which have deposited, and mixed with 3 litres of concentrated hydrochloric acid. The resulting brownish-red precipitate is quickly collected and extracted with cold water until it becomes pure grey in colour and the wash water is coloured a brownish-violet. One gram of cobalt chloride gives about 60 grms. of melanochloride.

When the grey mixture is treated with a hot soln. of silver nitrate, containing nitric acid, the filtrate, on cooling, deposits dark red crystals of the melanonitrate, and the mother-liquor gives a dark green nitrate which crystallizes out in large leaflets. If in preparing the melanochloride the temp. is kept below 5°, other products are formed in addition to those just indicated—*vide infra*.

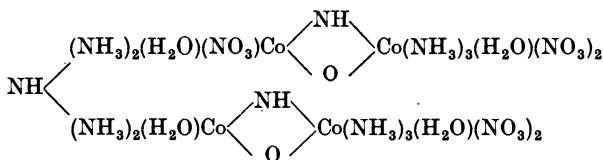
The first products of the oxidation of ammoniacal soln. of cobaltous salts by air, described by E. Frémy, and O. W. Gibbs as *oxycobaltiac salts*, were studied by G. Vortmann, A. Mylius, and by A. Werner and co-workers. According to E. Frémy, if the ammoniacal soln. be saturated with ammonium chloride, or,

according to G. Vortmann, if it be treated with alcohol, a brownish-black precipitate is obtained consisting of greenish-brown iridescent plates of **cobaltic peroxo-decamminotetrachloride**,  $[(\text{NH}_3)_5\text{Co}-\text{O}_2-\text{Co}(\text{NH}_3)_5]\text{Cl}_4$ . G. Vortmann noted that the dry salt or the aq. soln. is very unstable, and E. Frémy, that the crystals in contact with water give off oxygen. In this compound both the cobalt atoms are trivalent. If this salt be treated with hydrochloric acid, there is formed **cobaltic peroxo-decamminopentachloride**,  $[(\text{NH}_3)_5\text{Co}-\text{O}_2-\text{Co}(\text{NH}_3)_2]\text{Cl}_5$ , in which one of the cobalt atoms is quadrivalent, and the other one, trivalent. The exact nature of the salts with the  $\text{O}_2$ -linkage is yet unknown, since, amongst the possibilities, are the groups  $\text{Co.O.O.Co}$ , or :



The green, needle-like crystals are stable in air, but decompose at 110°. The salt was first obtained by L. Maquenne—*vide infra*, for the sulphate. G. Vortmann, and A. Werner and A. Mylius also prepared the salt. The aq. soln. of the salt is unstable. Boiling hydrochloric acid, and a reducing agent, converts it into the chloropentammine and a cobaltous salt; and ammonia convert it into chloropentammine and the hexammine. G. Vortmann obtained **mercuric cobaltic- $\mu$ -peroxo-decamminohenachloride**,  $[(\text{NH}_3)_5\text{Co}-\text{O}_2-\text{Co}(\text{NH}_3)_5]\text{Cl}_5 \cdot 3\text{HgCl}_2$ . According to A. Werner, if a soln. of the aquohydroxy-peroxo-ol-hexamminonitrate, or the corresponding sulphate, in water acidulated with acetic acid, be treated with a little conc. hydrochloric acid, small, greyish-black crystals of **cobaltic trichlorohydroxy-peroxo-hexamminochloride**,  $[\text{Cl}_2(\text{NH}_3)_5\text{Co}-\text{O}_2-\text{Co}(\text{NH}_3)_5(\text{OH})\text{Cl}]\text{Cl}$ , are formed. They are almost insoluble in water, and the salt is broken down when treated with liquid ammonia.

A. Werner and co-workers prepared what they called **cobaltic diozo-tri-imidodecammino-chloride**,  $(O_2)_2(NH)_3Co_4(NH_3)_{10}Cl_2 \cdot 2H_2O$ , by dissolving oxycobaltammine nitrate (300 grms.) in water (2 litres) at 50°, and, after filtration, diluting with an equal bulk of water, adding 4 litres of conc. hydrochloric acid, and then passing a current of air through the soln. for some hours. The black, crystalline precipitate of the crude chloride mixed with imido-hexammine chloride, after washing with alcohol and ether, is converted into the nitrate and re-converted into the chloride. It is a black, crystalline powder, sparingly soluble in cold water, more easily in warm water, is partially decomposed when heated with water at 60° to 70°, completely so when boiled, and gives brown, flocculent precipitates with platinic chloride and mercuric chloride. It is not decomposed by dil. acids or by conc. hydrochloric acid. The constitution of the diozo-salts is unknown. A. Werner and co-workers said that they probably have a constitution similar to that of the peroxo-salts. A comparison of their composition shows that they are formed by the combination of 2 mols. of the ozo-salt with elimination of 1 mol. of ammonia and the addition of 1 mol. of water. In the diozo-series, three imido-groups are present, and, considering the decomposition products obtained from the diozo-salts by the action of sulphurous, nitric, and nitrous acids, it is most probable that their constitution is expressed by a formula indicating the linking of 2 mols. of a peroxo-salt by an imido-group; thus, in the case of the nitrate :



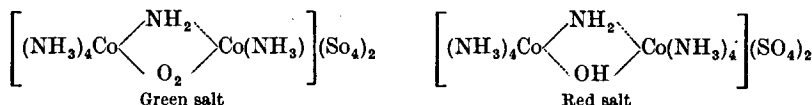
### *The $\mu$ -Amino-Salts.*

A. Werner,<sup>16</sup> and P. Wüst treated an aq. soln. of cobaltic aminohexamminopentamnitrate with ammonium chloride, and crystallized **cobaltic- $\mu$ -amino-decamminopentachloride**,  $[(\text{NH}_3)_5\text{Co}-\text{NH}_2\cdots\text{Co}(\text{NH}_3)_5]\text{Cl}_5$ , from the liquid feebly acidified with hydrochloric acid. The reddish-violet needles are soluble in water—at room temp. no part of the salt dissolves in about 80 parts of water. The salt

is stable at 85°, and is not decomposed by boiling water, but with hot, sulphuric or hydrochloric acids, it is resolved into the chloropentammine and the hexammine.

When an ammoniacal soln. of cobaltic nitrate is oxidized by a slow current of air, and then treated with an excess of sulphuric acid, an insoluble sulphate separates out. This has been called *Vortmann's fuscousulphate*, or *cobaltic fuscousulphate—fuscus*, dark—and it is one of a series of salts studied by E. Frémy, I. Fürstenberg, C. Schwenk, S. M. Jörgensen, M. Pieper, and G. Vortmann and O. Blasberg.

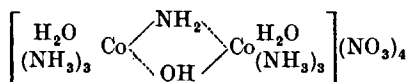
A. Werner showed that this product is not homogeneous, and by treatment with conc. hydrochloric acid, it furnishes a green, soluble salt, and a red salt which is sparingly soluble. The fuscousulphate can also be converted into nitrate, when the green salt is freely soluble in water, and the red salt is not so soluble. The fuscousulphate thus contains green **cobaltic- $\mu$ -amino-peroxo-octamminosulphate**, and red **cobaltic- $\mu$ -amino-ol-octamminosulphate** :



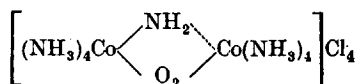
A. Werner and F. Salzer observed that if 10 grms. of this crude, red salt, covered with hydrochloric acid of sp. gr. 1.9, are kept at room temp., and the mixture is well-shaken at intervals, the salt passes into soln., the OH-bridge is destroyed, and brownish-violet, acicular crystals of **cobaltic chloroaquo- $\mu$ -amino-octamminochloride**,  $[(\text{H}_2\text{O})(\text{NH}_3)_4\text{Co}-\text{NH}_2\cdots\text{Co}(\text{NH}_3)_4\text{Cl}]\text{Cl}_4 \cdot 4\text{H}_2\text{O}$ , are formed. After 24 hrs., the crystals are collected, dissolved in cold water, and re-precipitated by hydrochloric acid. The salt is freely soluble in water; the soln. has an acidic reaction; and after standing some time, deposits the  $\mu$ -amino-ol-octamminochloride. When the soln. is boiled with hydrochloric acid, it forms pentammine and tetrammine salts. The freshly-prepared soln. gives characteristic precipitates with hydrochloroplatinic acid, mercuric chloride, and potassium iodide. The salt was studied by C. Schwenk, and A. Baselli. Y. Shibata investigated the absorption spectrum; and K. Matsuno, the action on the hydrosol of arsenic sulphide.

The structure of a number of cobaltammines has not yet been elucidated. There is the *cobaltic fuscocl chloride*—the *dihydrated cobaltic dihydroxyoctamminotetrachloride*,  $\text{Co}_2(\text{NH}_3)_8(\text{OH})_2\text{Cl}_4 \cdot 2\text{H}_2\text{O}$ , of E. Frémy, C. D. Braun, and G. Vortmann; and the fuscocl chloride—*pentahydrated cobaltic trioxo-octamminodichloride*,  $\text{Co}_2(\text{NH}_3)_8\text{O}_3\text{Cl}_2 \cdot 5\text{H}_2\text{O}$ , of E. Frémy.

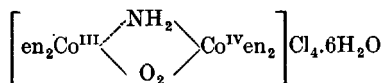
Cobaltic melanochloride was found by A. Werner, and A. Werner and F. Steinitzer, to furnish **cobaltic tetrachloro- $\mu$ -aminohexamminochloride**,  $[\text{Cl}_2(\text{NH}_3)_3\text{Co}-\text{NH}_2\cdots\text{Co}(\text{NH}_3)_3\text{Cl}_2]\text{Cl}$ , when dried at 60° to 65°; whereas if dried at the ordinary temp., it is **cobaltic trichloroaquo- $\mu$ -amino-hexamminodichloride**,  $[\text{Cl}_2(\text{NH}_3)_3\text{Co}-\text{NH}_2\cdots\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2$ . The crystals are violet-black, hexagonal plates; sparingly soluble in water, forming first a brown and then a red soln. The salt decomposes when heated with water; and silver nitrate converts it into diaquo- $\mu$ -amino-ol-hexamminonitrate :



According to A. Werner and F. Beddow, when a gram of Vortmann's salt is triturated with 6 to 8 c.c. of conc. hydrochloric acid, it forms a dark green mass which, dissolved in the smallest possible quantity of water, and filtered into conc. hydrochloric acid, yields **cobaltic  $\mu$ -amino-peroxo-octamminochloride** :

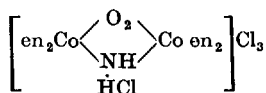


According to A. Werner and F. Beddow, and A. Werner and A. Grün, the dark green prisms are easily soluble in water; the aq. soln. has a neutral reaction, and it soon becomes acidic. The change is not so rapid in acidified soln. The 1 per cent. aq. soln. gives precipitates with sodium sulphate and phosphate, with potassium dichromate, chloroplatinite, and ferrocyanide, and with hydrochloroplatinic acid, but not with potassium iodide, cyanide, ferriyanide, and chloraurate. A. Werner, and P. Wüst found that the central  $\mu$ -amino-peroxo-group is very stable, and when the nitrate is warmed with 10 per cent. ethylenediamine all the ammonia can be replaced by ethylenediamine. If the resulting solution is then neutralized with nitric acid at the ordinary temp., a green salt is obtained; when the neutralization is carried out at low temp., a red salt is obtained. These salts only differ in their molecular composition, in that the former is anhydrous, whereas the latter contains 2 mols. of water of crystallization. The aq. soln. of the former is neutral, whereas that of the latter is acid. On warming a nitric acid soln. of the red salt, it changes into the green salt. The green salt is cobaltic  $\mu$ -amino-peroxo-quaterethylenediaminenitrate; during its preparation some decomposition occurs, and trisethylenediamine salts are formed. If the green salt is treated with potassium bromide, the corresponding bromide is produced, and if the bromide is treated with silver chloride, a soln. is produced which, when evaporated on the water-bath, furnishes dark green, cubic crystals of **cobaltic  $\mu$ -amino-peroxo-quaterethylenediaminechloride** :

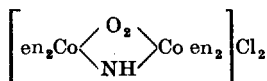


The salt is freely soluble in water, so that it cannot be separated from its aq. soln. by precipitation processes. The salt, over calcium chloride, decomposes with the loss of a mol. of water, and it loses all its water in the drying oven. If the groups ( $\text{en}_2\text{Co}^{\text{III}}$ ) and ( $\text{en}_2\text{Co}^{\text{IV}}$ ) be called A and B, it follows that four optically-active isomerides are theoretically possible—viz.,  $+A+B$ ,  $-A-B$ , and  $-A+B$ .

As first indicated, in connection with the preparation of cobaltic  $\mu$ -amino-peroxo-quaterethylenediaminenitrate, A. Werner showed that when the red salt is neutralized with nitric acid at a low temp., a red salt is obtained, which can be converted into the bromide, and, presumably, also into **cobaltic  $\mu$ -iminohydrochloro-peroxo-quaterethylenediaminechloride** :



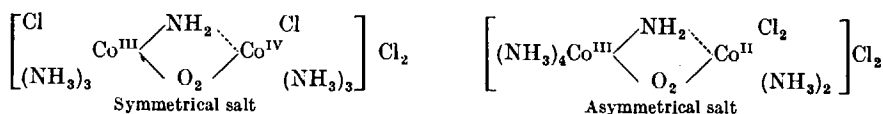
When the red and green salts are digested with ammonia, the mol. of acid is given off in the complex, and if the nitrate is triturated with a mixture of ammonia and sodium iodide, an iodide is formed, and when the aq. soln. of the iodide is shaken with silver chloride, **cobaltic  $\mu$ -imino-peroxo-quaterethylenediaminechloride** is formed :



Crystals of the chloride could not be obtained by evaporating the soln. The addition of potassium chloroplatinite to the aq. soln. gives a brownish-red precipitate of a double salt; and likewise with potassium chloraurate. The addition of hydrobromic acid and ammonium bromide produces the  $\mu$ -ammonium-peroxo-quaterethylenediaminebromide. If hydrochloric acid be added to the soln. of the chloride, it becomes red, owing to the formation of the ammonium-peroxo-salt, and then green, owing to its conversion to the isomeric amino-peroxo-salt.

A. Werner and R. Feenstra prepared **cobaltic iminobispyridineoctamminotetrachloride**,  $[(\text{NH}_3)_4\text{pyCo.NH.Co}(\text{NH}_3)_4\text{py}]_4\text{Cl}_4$ , by warming cobaltic dichloroaquatriamminochloride with water and pyridine. The yield is small. Conc. hydrobromic acid converts it into the bromide; it is easily soluble in water; and is precipitated from the soln. in golden-yellow needles by conc. hydrochloric acid. A. Werner is not satisfied with this formulation of the constitution.

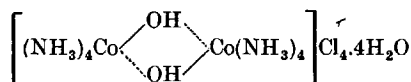
According to A. Werner, when an aq. soln. of cobaltic  $\mu$ -amino-ol-peroxo-hexamminochloride is warmed with conc. hydrochloric acid; or when a cold, conc. soln. of the corresponding nitrate is treated with conc. hydrochloric acid; or when an aq. soln. of  $\mu$ -amino-peroxo-octammino-salt is treated with ammonium chloride, and then saturated with hydrogen chloride, black crystals of symmetrical **cobaltic dichloro- $\mu$ -amino-peroxo-hexamminochloride** are formed. When a soln. of  $\mu$ -amino-peroxo-octamminonitrate is treated with an excess of ammonium carbonate instead of chloride, and hydrochloric acid is added to the cold liquid, dark olive-green crystals of an isomeric-form, namely, the asymmetrical salt, are found:



The asymmetrical salt is readily soluble in water, whereas the symmetrical salt is sparingly soluble. The action of liquid ammonia on the symmetrical form gives rise to  $\mu$ -amino-peroxo-octammine, showing that both the  $\mu$ -amino-peroxo-octammine, and the hexammine salts contain the same nucleus; whereas liquid ammonia with the asymmetrical salt yields  $\mu$ -amino-peroxo-ol-octammine, showing that it differs from the symmetrical form in the position of  $\text{NH}_3$ -groups.

### The Ol-Salts.

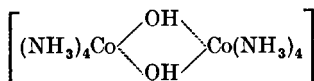
J. G. Gentele,<sup>17</sup> and S. M. Jørgensen prepared salts which A. Werner showed to be members of a series typified by **cobaltic diol-octamminochloride**:



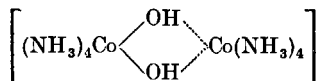
which was prepared by treating the product obtained by dehydrating hydroxy-aquotetramminosulphate with ammonium chloride on a water-bath. The salt was also prepared by J. V. Dubsy, and H. Frank. It furnishes small, dark red crystals, which lose 4 mols. of water at  $100^\circ$ . Y. Shibata measured the absorption spectrum; H. R. Kruyt and P. C. van der Willigen, the streaming potential at a glass capillary; and E. Rosenbohm, and L. C. Jackson, the magnetic properties. According to A. Werner, the salt is readily dissolved by water, forming a neutral soln. H. Frank found that when the diol-octamminochloride is treated with acetic acid, it forms the anhydrous salt; and with conc. hydrochloric acid, the green dichlorotetrammine. A. Werner found that the treatment of the salt with fuming hydrochloric acid, saturated at  $-12^\circ$ , yields the diaquotetrammine and dichlorotetrammine; J. V. Dubsy, that cold, conc. aq. ammonia, followed by the addition of alcohol, furnishes hydroxyaquotetramminochloride; and A. Werner, that ammonium oxalate, and potassium hydrophosphate give sparingly soluble, crystalline precipitates. K. Matsuno studied the flocculation of the hydrosol of arsenic sulphide by this salt.

A. Werner assumed that the two complex residues are combined together through the agency of the residual affinities of the oxygen atoms of the two OH-groups. The formula is in agreement with (i) the analyses; (ii) two mols.—*cis*-diaquotetrammine and *cis*-dichlorotetrammine—result from the decomposition of a mol. of the salt by hydrochloric acid; (iii) the acidic radicle is completely ionized in aq. soln. of the salt; and (iv) aq. soln. of the salt have a neutral reaction. The dihydrated cobaltic diol-octammine is a polymer of cobaltic hydroxyaquotetrammine. J. V. Dubsy regarded the salts formed by the loss of water from 2 mols. of hydroxyaquotetrammino-salts, say,  $[\text{Co}(\text{NH}_3)_4(\text{OH})(\text{H}_2\text{O})]\text{Cl}_2$ , to be the symmetrical diol-octammine; but the resolution of the diol-salts into *cis*-

diaquotetrammine and *cis*-dichlorotetrammine by mineral acids indicates an asymmetrical structure :



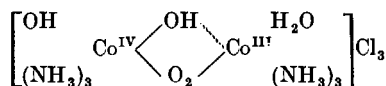
Symmetrical diol



Asymmetrical diol

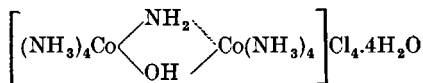
J. V. Dubsy, and H. Frank observed that when cobaltic hydroxyaquobisethylene-diaminedithionate is treated with acetic anhydride, and the product treated with ammonium chloride, **cobaltic diol-quaterethylenediaminechloride**,  $[\text{en}_2\text{Co} \ll (\text{OH})_2 \gg \text{Co en}_2]$ , is produced.

According to A. Werner, when cobaltic melanochloride is prepared at  $5^\circ$ , by exposing an ammoniacal soln. of cobaltous chloride to atmosphere air, there is formed, in addition to the products indicated above, cobaltic trichlorohydroxy-peroxy-hexamminochloride,  $[(\text{NH}_3)_3\text{Cl}(\text{OH})\text{Co}-\text{O}_2-\text{Co}(\text{NH}_3)_3\text{Cl}_2]\text{Cl}$ ; and when this product is treated with silver nitrate, it yields black nitrate in addition to the salts of  $\mu$ -amino-peroxy-ol-hexammine. The nitrate is converted into sulphate, and when the sulphate is treated with an excess of ammonium chloride and dil. acetic acid, it finally yields brown, soluble, acicular crystals of **cobaltic hydroxyaquo-peroxy-ol-hexamminochloride** :



In favour of this formula, A. Werner showed (i) Conc. nitric acid splits the salt into trinitratotriammine; conc. hydrochloric acid converts it into dichloroaquo-triammine; and a soln. of sodium iodide in acetic acid forms diol- $\mu$ -acetato-hexammine, all in agreement with the assumption that the 6  $\text{NH}_3$ -groups are equally shared by the 2 cobalt atoms; (ii) Liquid ammonia forms hexammine- and pentammine salts, indicating that no  $\text{NH}_2$ -bridge is present; (iii) Conc. sulphuric acid forms cobaltous sulphate, and a mixture of nitrogen and oxygen is evolved— $2\frac{1}{2}$  gram-atoms of oxygen for 2 gram-atoms of cobalt—and this agrees with the assumption that there is an  $\text{O}_2$ -bridge between trivalent and quadrivalent cobalt atoms; and (iv) The aq. soln. of the salt has an alkaline reaction, indicating that an OH-group is present. The second OH-group is assumed to be bridged, because it is indifferent to dil. mineral acids, and with conc. hydrochloric acid, it is replaced by chlorine to form trichlorohydroxy-peroxy-hexammine.

A. Werner, and A. Werner and A. Baselli prepared **cobaltic  $\mu$ -amino-ol-octamminochloride** :



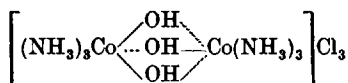
by heating the chloride, obtained from Vortmann's fuscousulphate, with hydrochloric acid on a water-bath, and adding alcohol to precipitate the small, blood-red, lustrous prisms; and also by rubbing the fuscousulphate with fuming hydrochloric acid, and precipitating the clear liquid with alcohol. A. Werner and F. Beddow also obtained it as follows :

Green cobaltic  $\mu$ -amino-peroxy-octammine nitrate, derived from the fuscousulphate, as indicated above, is warmed with a conc. aq. soln. of sulphurous acid until it becomes red, the cold mixture is treated with a few drops of nitric acid, and the violet precipitate which is obtained is triturated with conc. hydrochloric acid; the product is then dissolved in water, the hot, filtered soln. mixed with conc. hydrochloric acid, warmed on the water-bath for a short time, cooled, and mixed with an equal bulk of 90 per cent. alcohol. After being allowed to remain for 18 hrs., the  $\mu$ -amino-ol-octamminochloride separates as a dark red precipitate.



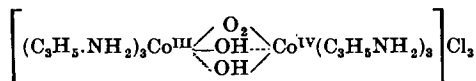
This compound was at first regarded as an imido-salt,  $[(\text{NH}_3)_4\text{Co}:\text{NH}.\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_4]\text{Cl}_4$ , but no imino-group could be detected; no salt formation took place either with acetic acid or dilute mineral acids; no acetylation took place by the action of acetic anhydride, and no nitroso-compound resulted from the action of nitrous acid. Further, the compounds in question were neutral in aq. soln. and not acid, as would be the case if the imino-formulation were correct. On the other hand, the amino-formulation accords well with the observed results. The cobalt atoms are all saturated with respect to co-ordination numbers. The complex radicle contains no water, and the salts do not, consequently, give an acid reaction when dissolved in water. The amino-group behaves like ammonia in metal ammonia compounds, being indifferent towards chemical reagents in the cold. The hydroxyl group, also, does not have the property of adding on hydrogen ions. The crystals of the salt were found by A. Werner to be slowly dissolved by cold water, to form a brownish-red soln.; warm water dissolves the salt more quickly. The aq. soln. decomposes with a protracted heating, but it is stable in soln. feebly acidified with acetic acid—36 parts of such a menstruum dissolves 1 part of salt at room temp. Hydrochloric acid converts it into chloropentamminochloride and dichlorotetramminochloride. The absorption spectrum was studied by Y. Shibata; and the flocculating action on the hydrosol of arsenic sulphide, by K. Matsuno.

According to A. Werner, and E. Birk, when cobaltic dichloroaquotriamminochloride is treated with a soln. of sodium hydroxide; or, according to A. Werner, when the cobaltic chlorodiaquotriamminosulphate is treated with soda-lye, and the product digested with barium chloride, there is formed **cobaltic triol-hexamminochloride** :



T. Das-Gupta and P. B. Sarkar obtained a better yield by using hexamethylene-tetrammine instead of soda-lye. The pale red or brownish-red, acicular crystals suffer no loss at  $80^\circ$ , but are decomposed at  $100^\circ$ . When decomposed with halogen hydracids, the salts of this family group give quantitative yields of triamminecobalt salts, indicating that three ammonia residues are attached to each cobalt atom. The acid residues are readily ionized, as each salt can be transformed into the others by double decomposition. Their aq. soln. are quite neutral to litmus, and hence the salts cannot be aquo-salts. They are isomeric with the black, cobaltic hexol-dodecammines, say,  $[\text{Co}(\text{OH})_6\{\text{Co}(\text{NH}_3)_4\}_3]\text{Cl}_6$ . The constitution of these salts was discussed by T. M. Lowry. K. Matsuno studied the flocculating action on the hydrosol of arsenic sulphide.

In studying the oxidation of an alcoholic soln. of cobaltous chloride containing a little allylamine, A. Pieroni and A. Pinotti observed that red crystals of a compound which they first regarded as an octiesallyllamine,  $\text{Co}(\text{C}_3\text{H}_5.\text{NH}_2)_8\text{Cl}_2$ , are formed, but later A. Pieroni represented it by the formula :  $[\text{Co}(\text{C}_3\text{H}_5.\text{NH}_2)_6(\text{O}_2)_2]\text{Cl}_2.\text{H}_2\text{O}_2$ . W. R. Bucknall and W. Wardlaw showed that the analysis, mol. wt. determinations from f.p. and conductivity data, agree with the assumption that the compound is **cobaltic diol-peroxo-sexiesallyllaminechloride** :



The sexiesallyllamine-salt was obtained in purple-red, acicular crystals. Conc. hydrochloric acid yields a dark green, insoluble substance, which on warming dissolves to a bluish-green soln. of cobaltous chloride and allylamine hydrochloride. The addition of conc. hydrochloric acid to an aq. soln. of the complex chloride produces a green soln. which reverts to the blue colour of cobaltous chloride only on warming. Sulphuric acid decomposes the complex ion and forms cobaltous sulphate. With silver nitrate soln. the complex chloride gives an immediate precipitate of silver chloride; together with a red precipitate, in conc. soln. of the complex nitrate. Ammonium sulphide immediately precipitates the

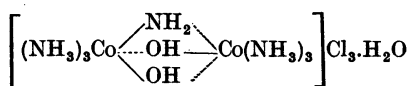
cobalt as sulphide. The complex salt reacts, on warming, with potassium iodide soln., with the liberation of iodine; with potassium bromide, however, no oxidation could be detected.

Analogous products were obtained by E. G. V. Percival and W. Wardlaw with propylamine, and benzylamine in place of allylamine. Red crystals of **cobaltic diol-peroxo-sexiespropylaminechloride**,  $[(C_3H_7.NH_2)_3Co \equiv (OH)_2O_2 \equiv Co(C_3H_7.NH_2)_3]Cl_3$ , were prepared by oxidizing dry cobaltous chloride in the presence of dry alcohol and dry *n*-propylamine. The cryoscopic and conductivity determinations of the aq. soln. indicate that four ions are formed. The complex chloride is very soluble in water, giving a neutral soln., and the addition of nitric acid produces, as in the case of the allylamine complex, an insoluble nitrate, all the chlorine having been displaced. Heated to 70°, an aq. soln. of the salt yields brown cobalt hydroxide, and propylamine is liberated. Ammonium sulphide immediately precipitates cobalt as sulphide. Conc. hydrochloric acid gives a green soln. The complex salt liberates iodine from potassium iodide soln. on warming. When cobaltous chloride is similarly treated in the presence of dry alcohol in dry benzylamine, **cobaltic triol-sexiesbenzylaminechloride**,  $[(C_6H_5.CH_2.NH_2)_3Co \equiv (OH)_3 \equiv Co(C_6H_5.CH_2.NH_2)_3]Cl_3$ , is formed. The colour of the salt is purple-red, and it is insoluble in water and alcohol. A suspension in water decomposed on being heated to 70°, with formation of cobalt hydroxide and the liberation of benzylamine and benzaldehyde. Cold, conc. nitric acid did not form a nitrate. Iodine was not liberated from potassium iodide soln. by this salt (unlike the peroxo-compounds) on warming in the presence of acetic acid. There is evidence of the formation of an analogous product with ethylamine, but not with methylamine, diethylamine, and piperidine. Thus, E. G. V. Percival and W. Wardlaw concluded that the oxidation of cobaltous chloride in alcohol in the presence of amines does not always produce polynuclear complexes. Only the primary amines, containing the  $CH_2.NH_2$ -group, have given successful results. Aniline, pyridine, and quinoline formed products which were not amenable to further oxidation by the method outlined above. Aniline, for example, gave an insoluble, blue compound of the composition  $CoCl_2.3C_6H_5NH_2$ , which on re-crystallization from alcohol yielded E. Lippmann and G. Vortmann's  $CoCl_2(C_6H_5.NH_2)_2(C_2H_5.OH)_2$ . This is taken to mean that there is probably formed a stable co-ordination compound,  $[CoCl_2(C_6H_5.NH_2)_2(C_2H_5.OH)_2]$ , which is not susceptible to atmospheric oxidation.

A. Werner prepared cobaltic diaquo- $\mu$ -amino-ol-hexamminonitrate,  $[(NH_3)_3(H_2O)Co \equiv (NH_2)(OH) \equiv Co(H_2O)(NH_3)_3](NO_3)_4.4H_2O$ , as follows:

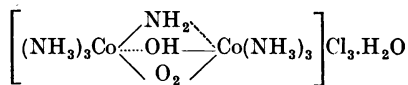
Twenty grams of melanochloride are triturated with a slightly acidic soln. of 36 grams of silver nitrate in 60 c.c. of water, and the mixture heated to 50° for some time. The silver chloride is collected and heated, at 80°, with separate quantities of 60 c.c. of very weak nitric acid, until it is colourless. To the united red extracts is added alcohol until incipient crystallization; on cooling in a freezing mixture, red crystals of the nitrate separate. After solution in water and re-precipitation with conc. nitric acid, garnet-red, flat, quadratic prisms are obtained.

When a warm soln. of this salt is saturated with ammonium bromide, the product triturated with moist silver chloride, and the aq. soln. treated with absolute alcohol, bright red, acicular crystals of **cobaltic  $\mu$ -amino-di-ol-hexamminochloride**:



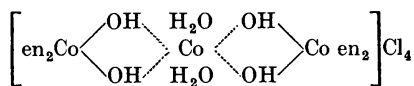
are formed. The salt is freely soluble in water, and the soln. has a neutral reaction. When warmed with nitric acid, this salt forms the nitratodiaquo- $\mu$ -amino-ol-hexamminonitrate; which, with liquid ammonia, passes into  $\mu$ -amino-ol-octamminonitrate, and then into  $\mu$ -amino-decamminonitrate. All this is taken to establish the hypothesis that the amine-group in the compound is bridged between the two cobalt atoms.

A. Werner and co-workers treated the black chloride, obtained by the action of silver nitrate on melanochloride, with silver nitrate, and saturated the filtrate with ammonium bromide. The resulting bromide was treated with silver chloride, and ammonium chloride, or alcohol, was added to the filtrate to precipitate **cobaltic  $\mu$ -amino-peroxo-ol-hexamminochloride** :



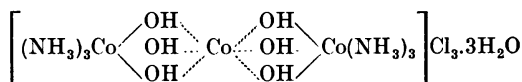
The salt can be re-crystallized from a conc. aq. soln. The water can be driven off by heat. The aq. soln. has a neutral reaction, and therefore it is not an aquo-salt, nor a hydroxy-salt. Fuming nitric acid furnishes trinitratotriammine, meaning that the six  $\text{NH}_3$ -groups are shared equally between the two cobalt atoms. Hydrochloric acid added to the conc. aq. soln. yields the dichloro- $\mu$ -amino-peroxo-hexamminochloride. The  $\mu$ -amino-peroxo-ol-hexammines are produced by the degradation of the  $\mu$ -amino-peroxo-octammines, and when an aq. soln. of this product is heated with ammonium chloride, and the liquid saturated with hydrogen chloride, cobaltic hexamminochloride separates out; and when reduced with potassium iodide and acetic acid, the  $\mu$ -amino-diol-hexammino-salt is formed, showing that the cobalt atoms are joined by an amine-group.

A. Werner and G. Jantsch found that the oxidation of aq. soln. of cobaltous salts containing some ethylenediamine, furnishes a series of quaterethylenediamine-salts. If cobaltous chloride is employed, and the oxidized liquor is treated with sodium chloride, **cobaltic-tetrol-quaterethylenediaminochloride** :



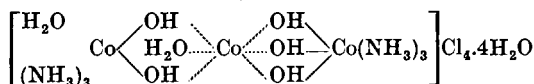
is formed along with cobaltic trisethylenediaminechloride. The latter is removed by washing the precipitate with water, and the tetrol-salt remains as a bright red powder with a faint blue tinge. When the tetrol-salt is treated with cold hydrochloric acid, no halogen is evolved, but a mol. of the salt yields a mol. of cobaltous chloride, and 2 mols. of *cis*-diaquobisethylenediaminechloride. The aquo-mols. in the 2 mols. of the diaquo-salt are not present in the parent salts, since these compounds do not react like diaquo-salts, but the complex of the parent salt contains 4 atoms of oxygen which must be employed in building up the molecule. The effect of hydrochloric acid shows that these compounds are formed by the union of a mol. of a cobaltous salt, with 2 mols. of a cobaltic dihydroxybisethylenediamine-salt. The aq. soln. has a neutral reaction, so that the OH-groups are bridged. They also contain 2 mols. of water retained by them in the dried state. The whole of the acid radicle is ionized in aq. soln. All this is in agreement with the formula assigned to the salt.

According to A. Werner, in preparing cobaltic triol-hexammino-sulphate by leaving cobaltic chlorodiaquotriamminosulphate in a soln. of ammonium bromide for several days, the reddish-brown mother-liquor, when strongly cooled, and mixed with conc. hydrochloric acid, gives a green precipitate. A soln. of this precipitate in water, acidulated with acetic acid, deposits an impure sulphate when treated with sulphuric acid. When this sulphate is treated with ammonium chloride, it furnishes dark green crystals of **cobaltic hexol-hexamminochloride** :

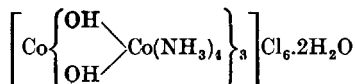


When this salt is decomposed by hydrochloric acid, dichloro-aquotriamminochloride, cobaltous chloride, and chlorine are formed, indicating that the six  $\text{NH}_3$ -groups

are shared equally by 2 cobalt atoms, and chlorine is liberated as the third cobalt atom passes from the tervalent to the bivalent form. There is no evidence of any amino-linkages. All three acid-radicles are ionogenic. The salt forms with water a yellowish-brown soln. When soln. of this salt are treated with hydrochloric acid, in the cold, one of the ol-linkages is destroyed, and there are formed green crystals of **cobaltic diaquo-pentol-hexamminochloride**,

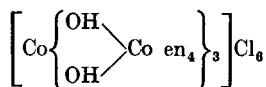


S. M. Jörgensen prepared a series of salts which he called *anhydrobasische Tetrammin-Diaquodiamminkobaltsalze*; and A. Werner, *Dodekammine-hexol-tetrammin-kobalt (111)-salze*. S. M. Jörgensen prepared the chloride—**cobaltic hexol-dodecamminochloride**:



by dissolving chloroaquotetramminochloride in dil. aq. ammonia, and after allowing the mixture to stand in a closed flask for 24 hrs., adding 90 per cent. alcohol. The salt is precipitated in small, hexagonal tablets, which are dark violet, almost black in colour. A. Werner obtained the salt in this way, and also by warming the sulphate of the series with a soln. of barium chloride, and treating the filtered, dark brown liquid with alcohol. E. Birk prepared the salt by dissolving 10 grms. of cobaltic triaquotriamminochloride in 10 c.c. of water, adding slowly 3.1 c.c. of a 10 per cent. aq. soln. of potassium hydroxide, and then 30 to 50 c.c. of alcohol. Y. Shibata measured the absorption spectrum. S. Berkman and H. Zocher found the magnetic susceptibility to be  $-0.22 \times 10^{-6}$  mass unit. According to S. M. Jörgensen, the salt is freely soluble in water, but after a time the aq. soln. decomposes, and deposits a dark grey, amorphous mass. Y. Shibata also noted the hydrolysis of the salt in aq. soln. S. M. Jörgensen observed that the salt is decomposed when gently warmed with 1:1-hydrochloric acid, to furnish cobaltic chloroaquotetramminochloride, cobaltous chloride, chlorine, ammonium chloride, and water; and when heated with the 1:2-acid, it is almost completely converted into dichlorotetramminochloride. A freshly-prepared, 1 per cent. aq. soln. gives characteristic precipitates with many metal salts, and acids—*e.g.*, brown crystalline precipitates with dil. nitric acid, hydrofluosilicic acid, ammonium sulphate, and sodium dithionate; grey or yellow precipitates with mercuric chloride, with potassium chromate or chloroplatinite, and with sodium chloraurate, or chloroplatinate; sodium pyrophosphate gives a brown turbidity; and sodium hydrophosphate gives no precipitate. K. Matsuno studied the flocculating action on the hydrosol of arsenic sulphide.

In addition to the ammonia-series of hexol-dodecammines, prepared by S. M. Jörgensen, there is a similar ethylenediamine-series, prepared by A. Werner. Brown, soluble, acicular crystals of **cobaltic hexol-sexiesethylenediaminechloride**:



were obtained by exposing a soln. of cobalt chloride and ethylenediamine to atmospheric oxidation. When dissolved in conc. hydrochloric acid, *cis*-diaquobis-ethylenediaminechloride is formed, and similarly with hydrobromic acid; when evaporated with dil. hydrochloric acid, *trans*-dichlorobisethylenediaminechloride is produced; and when treated with a soln. of potassium hydroxide, *cis*-hydroxy-aquobisethylenediaminechloride.

S. M. Jörgensen represented the ammonia-series of these salts by formulæ of

the type:  $(\text{HO})(\text{H}_2\text{O})_2(\text{NH}_3)_2\text{Co.O.Co}(\text{NH}_3)_4\text{Cl}_2$ , but A. Werner's objections were as follow:

(i) The salts cannot contain HO directly attached to cobalt, since they do not yield aquo-salts by treatment with mineral acid; (ii) in the chloride, the presence of chlorine directly attached to cobalt is contrary to the fact that this salt is converted into a halogen-free sulphate by the action of soluble sulphates; (iii) the estimation of the products of decomposition of these salts by hydrochloric or hydrobromic acid leads to results contrary to those anticipated by S. M. Jörgensen's formula. Thus, the sulphate of the ammonia series yields 81.1 per cent. of diaquatetramminecobalt chloride, and the nitrate of the ethylenediamine series, 80.71 per cent. of 1:6-dichlorodiethylenediaminecobalt nitrate, whereas the amounts calculated from S. M. Jörgensen's formula are 68.1 per cent. and 54.6 per cent. respectively. If the mol. formulæ of these complex salts are doubled and A. Werner's constitutional formula is adopted, the observed percentages in the preceding decompositions agree well with the calculated values; (iv) the estimation of the chlorine evolved by the action of cold conc. hydrochloric acid on salts of either series agrees well with the theory that in the molecule of these salts, 4 cobalt atoms are present, one of which passes from the trivalent to the bivalent state during the decomposition. According to S. M. Jörgensen's formula, the products of decomposition must contain one cobalt atom in the form of a tetrammine salt, and one cobalt atom as a diammine salt; the latter, in spite of numerous attempts, cannot be detected; (v) the sulphate of the ammonia series is decomposed by dil. sulphuric acid, yielding oxygen, and by conc. sulphuric acid, evolving oxygen and nitrogen in quantities which agree with those calculated from A. Werner's formula.

A. Classen and B. Zahorsky<sup>18</sup> described a **cobaltosic pyridine**,  $\text{CoCl}_2 \cdot \text{CoCl}_3 \cdot 5\text{C}_5\text{H}_5\text{N}$ .

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### § 17. The Cobaltic Ammines

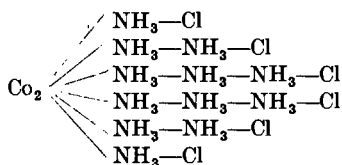
Es giebt wohl kaum eine andere Körperklasse, über die es viel geschrieben worden ist, wie über diese metallhaltigen Ammoniake.—C. W. BLOMSTRAND (1869).

In 1798, B. M. Tassaert,<sup>1</sup> in his paper, *Analyse du cobalt de Tunaberg*, mentioned the formation of compounds of ammonia with the salts of cobalt, and some isolated observations on the subject were made during the first half of the nineteenth century by W. Beetz, E. H. Dingler, L. Gmelin, H. Hess, C. H. Pfaff, J. L. Proust, C. F. Rammelsberg, and G. C. Winkelleblech. The subject began to attract attention about the middle of the nineteenth century, and memoirs on the cobalt-ammonia compounds were subsequently published by C. H. D. Bödeker, C. D. Braun, E. Carstanjen, F. Claudet, C. E. Claus, E. Frémy, J. G. Gentile, F. A. Genth, O. W. Gibbs and F. A. Genth, W. Gregory, J. M. Krok, C. Künzel, E. J. Mills, J. B. Rogojsky, F. Rose, H. Schiff, A. Terreil, and C. Weltzien.

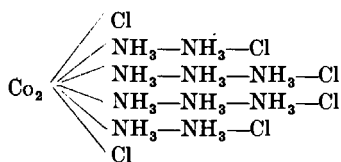
Meanwhile, analogous compounds of chromium, and some of the platinum metals had been investigated, and it was recognized that the **metal-ammonia bases**, as they were called, formed a special department in chemistry. Attempts were made by C. H. D. Bödeker, O. W. Gibbs and F. A. Genth, H. Schiff, C. Weltzien, etc., to bring order into the chaotic accumulation of facts. It was recognized that certain groups of atoms acted as bases, and each of these bases in turn formed, with various acidic radicles, a series of salts. E. Frémy named the different bases he had studied after the dominant colour of some of the leading members of the series. Although this method of naming the compounds had ultimately to give way to a more systematic nomenclature, yet it is often employed in order to evade using the more ponderous systematic names. Thus, the members of a family of salts with six  $\text{NH}_3$ -groups per atom of cobalt were called *luteo-salts*—from *luteus*, yellow—in allusion to the yellow colour of the chloride, sulphate, and nitrate; the members of one of the families with five  $\text{NH}_3$ -groups per atom of cobalt were called *purpureo-salts*—from *purpura*, purple—in allusion to the purple tint of the chloride, sulphate, and nitrate; and the members of one of the families, with four  $\text{NH}_3$ -groups per atom of cobalt were called *praseo-salts*—from *πρασῖος*, leek-green—in allusion to the dominant colour of the salts.

In 1869, C. W. Blomstrand<sup>2</sup> suggested a system of chain formulæ to represent the structure of these compounds; it was based on the electrochemical or dualistic theory of J. J. Berzelius—1. 8, 16—and on the recognized valencies of the contained elements. At that time, cobaltic chloride was represented by the formula  $\text{Co}_2\text{Cl}_3$ ,

and, accordingly, a pair of cobalt atoms was considered to be a kind of sexivalent radicle. Instead of using the symmetrical formula  $(\text{Cl}-\text{NH}_3-\text{NH}_3)_3 \equiv \text{Co}_2 \equiv (\text{NH}_3-\text{NH}_3-\text{Cl})_3$ , where Cl is employed to represent the univalent radicle as well as an atom of chlorine, he suggested for the dodeca-ammonia and deca-ammonia bases, respectively :

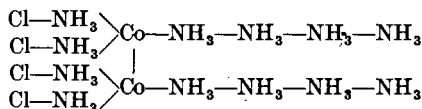


Luteo-salt

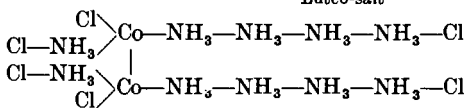


Purpureo-salt

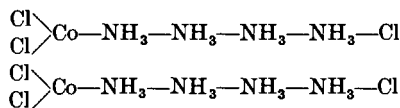
in order to explain why, in passing from the luteo-salt to the purpureo-salt, two of the six acidic Cl-radicles of the purpureo-salts are no longer susceptible to, say, silver nitrate, which immediately attacks all the six acidic radicles of the luteo-salts. It was assumed that two of the Cl-radicles in close contact with the cobalt atoms were not so susceptible to attack as were those with intervening  $\text{NH}_3$ -groups. The removal of two more  $\text{NH}_3$ -groups to furnish the praseo-salts resulted in the removal of two more acidic radicles from the zone of attack. S. M. Jørgensen therefore modified C. W. Blomstrand's formulæ to :



Luteo-salt

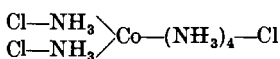
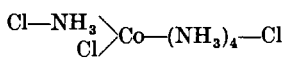
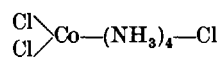


Purpureo-salt

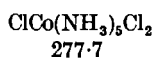


Praseo-salt

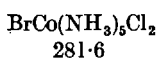
Molecular weight determinations by L. F. Nilson and O. Pettersson, and J. Petersen on the analogous chromic-ammonia salts, and of A. Werner and C. Herty, and A. Werner and A. Miolati on the cobaltic-ammonia salts, showed that the doubled formulæ must give way to the simpler chain formulæ :

Luteo-salt— $\text{Co}(\text{NH}_3)_6\text{Cl}_2$ Purpureo-salt— $\text{ClCo}(\text{NH}_3)_5\text{Cl}_2$ Praseo-salt— $\text{Cl}_2\text{Co}(\text{NH}_3)_4\text{Cl}$ 

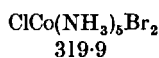
These formulæ explain how it is that in metathetical reactions, one chlorine atom remains associated with the cobalt and  $\text{NH}_3$ -groups in the penta-ammonia compounds, and two chlorine atoms, in its tetra-ammonia compounds ; how conc. sulphuric acid will remove only two of the three Cl-atoms in the penta-ammonia salts, and only one of the three Cl-atoms in the tetra-ammonia salts ; and why, if a bromine be substituted for chlorine in different ways, say, in the penta-ammonia salts, the mol. vol. of the compounds are different. Thus :



277.7

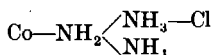


281.6



319.9

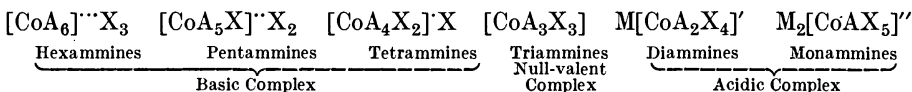
S. M. Jørgensen also found that the  $\text{NH}_3$ -groups may be replaced by aqua- or  $\text{H}_2\text{O}$ -groups, as well as by pyridine, and other groups. He then inquired if the chains of ammonia radicles are straight or branched. If there are two branches, the one labile hydrogen must behave differently, since the chain in the one case is, say,  $\text{Co}-\text{NH}_3-\text{NH}_3-\text{NH}_3-\text{Cl}$ , and in the other case, say,



He found that since with pyridine no labile hydrogen atoms and no forked chains are possible when pyridine groups are substituted for  $\text{NH}_3$ -groups in the compounds, the resulting metal-pyridine salts behave just like the metal-ammonia salts, and this makes it highly probable that the metal ammonias do not contain the  $\text{NH}_4$ -group, and that the  $\text{NH}_3$ -chains are not branched.

The conductivity determinations showed that these different families of salts contain cobalt as part of a series of complex cations which are respectively ter-, bi-, and uni-valent, according as the complex cation has none, one, or two  $\text{NH}_3$ -groups replaced by acidic radicles, which then become part of the complex cation. If another substitution of the  $\text{NH}_3$ -groups be made, as in the trinitrite,  $(\text{NH}_3)_3\text{Co}(\text{NO}_2)_3$ , the complex is null-valent. If still another  $\text{NH}_3$ -group be displaced by the acidic radicle, the complex is no longer catonic, or basic, but rather is anionic or acidic, since it is univalent and forms salts with the bases. The replacement of four  $\text{NH}_3$ -groups thus furnishes a univalent anion; and in an analogous manner, the replacement of a fifth  $\text{NH}_3$ -group, yields a bivalent anion.

The term **metal-ammines**, or simply **ammines**, came to be employed for the metal-ammonias. Ammine is the name applied specifically to an  $\text{NH}_3$ -group; and generally to  $\text{NH}_3$ - or equivalent groups. Then followed A. Werner's co-ordination theory—8, 49, 19—in which no very definite hypothesis was made respecting the grouping of the complex anions or cations within the complex. This hypothesis enabled nearly all the known complex metal-ammonia compounds to be classified in a consistent manner. In A. Werner's classification, the cobalt ammines are arranged in two groups, according as the nucleus has one or more cobalt atoms. If A be employed to represent an  $\text{NH}_3$ - or an equivalent group, and X a univalent acidic radicle, and M a univalent base, there are five families in the group with one cobalt atom in the nucleus to be considered:



In contrast with the **Blomstrand and Jörgensen's chain theory**, A. Werner's system of classification has been called **Werner's nucleus theory**, or, for reasons indicated 8, 49, 19, **Werner's co-ordination theory**. Speculations as to (i) the disposition of the groups of radicles about the central cobalt atom, and (ii) the nature of the different kinds of valency bonds, came later—*vide* the platinum ammines. The constitution was discussed in a number of books:

O. Angern, *Die Ammine des Kobalts*, in *Gmelin's Handbuch der anorganischen Chemie*, Berlin, 58, 1930; A. E. van Arkel and J. H. de Boer, *Chemische Bindung als elektrostatische Erscheinung*, Leipzig, 1931; W. A. Noyes, *Journ. Amer. Chem. Soc.* 55, 4889, 1933; P. Pfeiffer, *Organische Molekülverbindungen*, Stuttgart, 1922; F. Reitzenstein, *Ueber die verschiedenen Theorien zur Erklärung der Konstitution der Metallammoniaksalze*, Würzburg, 1898; *Zeit. anorg. Chem.*, 18, 152, 1898; B. Schwarz, *Chemie der anorganischen komplexverbindungen*, Berlin, 1920; London, 1923; N. V. Sidgwick, *The Electronic Theory of Valency*, Oxford, 1927; J. D. M. Smith, *Chemistry and Atomic Structure*, London, 1924; M. M. J. Sutherland, *The Metal Ammines*, London, 1928; W. Thomas, *Complex Salts*, London, 1924; G. Urbain and A. Sénéchal, *Introduction à la chimie des complexes*, Paris, 1913; R. Weinland, *Einführung in die Chemie der Komplex-Verbindungen*, Stuttgart, 1919; A. Werner, *Neuere Anschauungen auf dem Gebiete der anorganischen Chemie*, Braunschweig, 1923; G. Wittig, *Stereochemie*, Leipzig, 1930.

The following is an outline sketch of the cobaltic ammines in accord with the plan adopted with the chromic ammines—11, 60, 24.

#### A.—Compounds with one Cobalt atom in the nucleus.

I.—**The hexammine family**, or compounds of the tervalent basic group:  $[\text{CoA}_6]^{+++}$ .

(i) **Hexammines**,  $[\text{Co}(\text{NH}_3)_6]\text{X}_3$ . These salts are the so-called **cobaltic luteo-salts**—*luteus*, yellow. They include (1) Hydroxide; (2)

Fluoride, and its double salts with boron, titanium, and vanadium fluorides; (3) Hydrofluoride; (4) Chloride and its ammonia addition compounds, and double salts with the copper, zinc, cadmium, mercuric, tin, lead, antimony, bismuth, gold, platinum, iridium, ruthenium, and rhodium chlorides; (5) Chlorofluoride; (6) Chlorite; (7) Chlorate; (8) Perchlorate; (9) Chloroperchlorate; (10) Bromide and its ammonia addition compounds, and double salts with cadmium, mercury, lead, bismuth, gold, and iridium bromides; (11) Hydrobromate; (12) Iodide and its ammonia addition compounds, and double salts with mercury and bismuth iodides; (13) Polyiodides; (14) Chlorohydroiodate; (15) Sulphite; (16) Chlorosulphite; (17) Sulphate, and double salts with ammonium thallium, cerium, and lanthanum sulphates; (18) Hydrosulphates; (19) Chlorosulphate, and double salts with ammonium, and mercury sulphates; (20) Chloratosulphate; (21) Perchloratosulphate; (22) Bromosulphate, the double salt with gold; (23) Iodosulphate; (24) Sulphatopersulphate; (25) Chlorothiosulphate; (26) Selenate, and the double salt with ammonium; (27) Hydroselenate; (28) Chloroselenate; (29) Bromoselenate; (30) Iodoselenate; (31) Selenatopersulphate; (32) Nitrite; (33) Nitrate; (34) Hydronitrate; (35) Fluonitrate; (36) Iodonitrate; (37) Sulphatonitrate; (38) Amidosulphonate; (39) Imidosulphate; (40) Nitrilosulphonate; (41) Hydroxylaminosulphate; (42) Carbonate; (43) Hydrocarbonate; (44) Chlorocarbonate; (45) Fluosilicate; (46) Hypophosphate; (47) Orthophosphate; (48) Hydrophosphate; (49) Pyrophosphate, and double salts with sodium pyrophosphate; (50) Hypopyrophosphate; (51) Chlorometaphosphate; (52) Chromate; (53) Dichromate; (54) Chlorochromate; (55) Bromochromate; (56) Iodochromate; (57) Molybdates; (58) Iodomolybdate; (59) Tungstates; (60) Permanganate; (61) Chloro-permanganate; (62) Bromopermanganate; (63) Acetate; (64) Oxalate, and double salt with cadmium and cobalt oxalates; (65) Hydroxalate; (66) Chloroxalate; (67) Oxalatochromate; (68) Picrate; (69) Dipicrylamine; (70) Nitroso- $\beta$ -naphtholoxide; (71) 2:4-Dinitro- $\alpha$ -naphtholsulphonate; (72) *m*-Nitrobenzeneazosalicylate; (73) 2:4-Dinitro- $\alpha$ -naphtholsulphonates; (74) Naphthalene- $\beta$ -sulphonate; (75) Hexacyanoferrite; (76) Hexacyanoferrate; (77) Thiocyanate, and double salts with silver, mercury, and platinum thiocyanates; (78) Trisulphitocobaltate; (79) Hexanitrocobaltate; (80) Tetranitrodiamminocobaltate; (81) Trioxalatocobaltate; (82) Dinitro-oxalatodiamminocobaltate; and (83) Potassium and ammonium octoborates.

- (ii) *Hexahydroxylamines*,  $[\text{Co}(\text{NH}_2\text{OH})_6]\text{X}_3$ , include (1) Chloride; (2) Bromide; (3) Sulphate; (4) Nitrate; and (5) Oxalate.
- (iii) *Hydroxylaminebisethylenediamineammines*,  $[\text{Co}(\text{NH}_3)(\text{NH}_2\text{OH})\text{en}_2]\text{X}_3$ , represented by the dextro- and lævo-forms of (1) Hydroxide; (2) Chloride; (3) Perchlorate; (4) Bromide; (5) Iodide; (6) Dithionate; and (7) Nitrate.
- (iv) *Trisethylenediamines*,  $[\text{Co en}_3]\text{X}_3$ , include (1) Hydroxide; (2) Fluoride; (3) Chloride, and double salts with sodium, copper, mercury, cobalt, bismuth, nickel, iridium, and platinum chlorides; (4) Perchlorate; (5) Bromide, and a double salt with mercury bromide; (6) Iodide, and a double salt with silver iodide; (7) Polyiodide; (8) Sulphate; (9) Hydrosulphate; (10) Chlorosulphate; (11) Thiosulphate; (12) Selenate; (13) Hydroselenate; (14) Nitrite; (15) Nitrate; (16) Tartrate; (17) Chlorotartrate; (18) Bromotartrate; (19) Trioxalatochromate; (20) Trioxalatocobaltate; (21) Bromodimethyl-

- succinate; (22) Thiocyanate; (23) Trithiocyanatomercurate (24) Hexacyanochromate.
- (v) *Trispropylenediamines*, or *triscyclopentanediamines*,  $[\text{Co pn}_3]\text{X}_3$ , include (1) Hydroxide; (2) Chloride; (3) Chlorate; (4) Perchlorate; (5) Bromide; (6) Iodide; (7) Nitrate; (8) Thiocyanate; (9) Hexacyanochromate; (10) Hexacyanoferrate; (11) Hexacyanocobaltate; (12) Trioxalatochromate; and (13) Chlorotartrate.
- (vi) *Trisbutylenediamines*,  $[\text{Co bn}_3]\text{X}_3$ , represented by (1) Bromide; (2) Iodide; and (3) Thiocyanate.
- (vii) *Trisphenylenediamines*,  $[\text{Co(o-C}_6\text{H}_8\text{N}_2)_3]\text{X}_3$ , are represented by the chloride.
- (viii) *Bistriaminopropanes*,  $[\text{Co}(\alpha\beta\gamma\text{-C}_3\text{H}_{11}\text{N}_3)_2]\text{X}_3$ , include (1) Chloride, and the double salt with platinum chloride; (2) Iodide; (3) Thiocyanate; and (4) Camphorate.
- (ix) *Bisethylenediaminediammines*,  $[\text{Co}(\text{NH}_3)_2\text{en}_2]\text{X}_3$ , include (1) Chloride, and double salts with mercury, cobaltous, gold, and platinum chlorides; (2) Bromide; (3) Iodide; (4) Polyiodide; (5) Dithionate; (6) Nitrate; (7) Chloroxalate; (8) Iodoxalate; and (9) Bromocamphorsulphonate.
- (x) *Bispropylenediaminediammines*,  $[\text{Co}(\text{NH}_3)_2\text{pn}_2]\text{X}_3$ , include (1) Chloride, and double salts with gold, mercury, tin and cobaltous chlorides; (2) Bromide; (3) Iodide; (4) Dithionate; (5) Nitrate; and (6) Dichromate.
- (xi) *Ethylenediaminedicyclopentanediamines*,  $[\text{Co en}(\text{C}_5\text{H}_{12}\text{N}_2)_2]\text{X}_3$ , represented by the (1) Chloride; (2) Bromide; and (3) Iodide.
- (xii) *Bisethylenediaminepropylenediamine*,  $[\text{Co en}_2\text{pn}]\text{X}_3$ , include (1) Hydroxide; (2) Bromide; (3) Iodide; (4) Thiocyanate; (5) Hexacyanochromate; (6) Hexacyanocobaltate; (7) Trioxalatochromate; and (8) Trioxalatocobaltate.
- (xiii) *Bisethylenediaminecyclopentaminodiamines*,  $[\text{Co en}_2(\text{C}_5\text{H}_{12}\text{N}_2)]\text{X}_3$ , include (1) Chloride; (2) Perchlorate; (3) Bromide; (4) Iodide; (5) Nitrate; and (6) Bromotartrate.
- (xiv) *Bisethylenediaminepyridinediammines*,  $[\text{Co}(\text{NH}_3)\text{en}_2\text{py}]\text{X}_3$ , represented by the bromide.
- (xv) *Bisethylenediamine- $\alpha$ -phenanthrolines*,  $[\text{Co en}_2(\text{C}_{12}\text{H}_8\text{N}_2)]\text{X}_3$ , include (1) Chlorate; (2) Bromide; (3) Iodide; (4) Sulphate; (5) Chlorosulphate; (6) Nitrate; (7) Tartrate; and (8) Bromocamphorsulphonate.
- (xvi) *Bistriaminotriethylaminesesizesethylenediamines*,  $[\text{Co en}_6(\text{C}_6\text{H}_{18}\text{N}_4)_2]\text{X}_3$ , include (1) Chloride; (2) Chlorate; (3) Perchlorate; (4) Iodide; (5) Iodate; (6) Sulphate; (7) Chlorosulphate; (8) Dithionate; (9) Nitrate; and (10) Iodotartrate.
- (xvii) *Trisdiaminopentanes*,  $[\text{Co ptn}_3]\text{X}_3$ , represented by the  $\alpha\beta\delta$ - and the  $\beta\beta\delta$ -salts, (1) Chloride; (2) Perchlorate; (3) Bromide; (4) Iodide; (5) Dithionate; (6) Nitrate; and (7) Bromo- $\alpha$ -tartrate.
- (xviii) *Bisethylenediaminodiaminopentane*,  $[\text{Co en}_2\text{ptn}]\text{X}_3$ , represented by the bromide.
- (xix) *Aquopentammines*,  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{X}_3$ , are the **cobaltic roseo-salts**—from *rosa*, a rose—of E. Frémy, and were so called in allusion to the red colour of the chloride, sulphate, and nitrate. They include (1) Hydroxide; (2) Fluoride; (3) Hydrofluoride; (4) Chloride, and its ammonia addition compounds, and double salts with the chlorides of zinc, cadmium, mercury, gold, iridium, and platinum; (5) Chlorite; (6) Chlorate; (7) Perchlorate; (8) Bromide and ammonia addition compounds, as well as double salts with the chlorides of cadmium, mercury, gold, iridium, and platinum; (9) Iodide, and ammonia addi-

tion compounds, as well as a double salt with the iodide of mercury ; (10) Sulphite, and a double salt with sodium sulphite ; (11) Trisulphitocobaltate ; (12) Sulphate, and a double salt with sodium phosphate ; (13) Hydrosulphate ; (14) Chlorosulphate ; (15) Chloratosulphate ; (16) Perchloratosulphate ; (17) Bromosulphate ; (18) Iodosulphate ; (19) Selenate ; (20) Nitrate ; (21) Hydronitrate ; (22) Iodonitrate ; (23) Sulphatonitrate ; (24) Amidosulphonate ; (25) Imidosulphonate ; (26) Nitrilosulphonate ; (27) Hydroxylaminetrisulphonate ; (28) Carbonate ; (29) Orthophosphate ; (30) Hydrophosphate ; (31) Pyrophosphate ; (32) Hydropyrophosphate ; (33) Vanadate ; (34) Dichromate ; (35) Molybdates ; (36) Tungstates ; (37) Oxalate ; (38) Hydroxalate ; (39) Trioxalatocobaltate ; (40) 2 : 4 and 2 : 6-Dinitrophenol ; (41) Picrate ; (42) Dipicrylamine ; (43) 2 : 4-Dinitro- $\alpha$ -naphtholsulphonate ; (44) Naphthalene- $\beta$ -sulphonate ; (45) Nitrato-tartrate ; (46) Nitratosuccinate ; (47) Nitroadipate ; (48) Nitrato-fumarate ; (49) Nitratomethionate ; (50) Hexacyanochromate ; (51) Tetra isothiocyanatodiamminochromate ; (52) Hexacyanoferrate ; (53) Hexacyanocobaltate ; (54) Potassium and ammonium octoborates ; (55) Ammonium cobaltic aquopentammineoctoborate.

(xx) *Aquobisethylenediamineammines*,  $[\text{Co}(\text{NH}_3)_n(\text{H}_2\text{O})]\text{X}_3$ , include (1) Chloride as double salts with platinum ; (2) Bromide ; (3) Iodide ; and (4) Nitrate.

(xxi) *Aquopyridinetetrammines*,  $[\text{Co}(\text{NH}_3)_4\text{py}(\text{H}_2\text{O})]\text{X}_3$ , represented by the nitrate.

(xxii) *Aquodipyridinetriammines*,  $[\text{Co}(\text{NH}_3)_3\text{py}_2(\text{H}_2\text{O})]\text{X}_3$ , represented by the (1) Chloride ; and (2) Bromide.

(xxiii) *Diaquotetrammines*,  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})]\text{X}_3$ . These salts have been called the **cobaltic roseotetrammine-salts**, in allusion to the colour of the chloride, etc. The cobaltic roseo-salts are the aquopentammines. They include (1) Hydroxide ; (2) Chloride ; (3) Bromide ; (4) Iodide ; (5) Sulphate, and a basic sulphate ; (6) Hydrosulphate ; (7) Perchloratosulphate ; (8) Chlorosulphate, represented by a double salt with platinum ; (9) Bromosulphate, and double salts with gold and iridium ; (10) Selenate ; (11) Nitrate ; (12) Amidosulphonate ; (13) Orthophosphate ; (14) Pyrophosphate ; (15) Molybdate ; (16) Acetate ; (17) Oxalate ; (18) Trioxalatocobaltate ; (19) Picrate ; (20) Naphthalene- $\beta$ -sulphonate ; and (21) Hexacyanocobaltate.

(xxiv) *Diaquobisethylenediamines*,  $[\text{Co en}_2(\text{H}_2\text{O})_2]\text{X}_3$ , include (1) Hydroxide ; (2) Chloride ; (3) Bromide ; (4) Iodide ; (5) Sulphate ; (6) Dithionate ; (7) Nitrate ; and (8) Thiocyanate.

(xxv) *Diaquobis trimethylenediamines*,  $[\text{Co tr}_2(\text{H}_2\text{O})_2]\text{X}$ , represented by the Nitrate.

(xxvi) *Diaquobispyridinediammines*,  $[\text{Co}(\text{NH}_3)_2\text{py}_2(\text{H}_2\text{O})_2]\text{X}_3$ , include (1) Chloride ; (2) Bromide ; (3) Hydrosulphate ; (4) Dithionate ; (5) Hydroselenate ; and (6) Nitrate.

(xxvii) *Triaquotriammines*,  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_3]\text{X}_3$ , include (1) Chloride, and the double salt with platinum ; (2) Perchloratosulphate ; and (3) Nitrate.

(xxviii) *Tetraquodiammines*,  $[\text{Co}(\text{NH}_3)_2(\text{H}_2\text{O})_4]\text{X}_3$ , include (1) Chloride ; and (2) Nitrate.

# I.—The Pentammine family, or compounds of the bivalent basic group : $[\text{CoA}_2\text{X}]^{+}$ .

(a) *Pentammines with Univalent Radicle in the Complex.*

(i) *Hydroxypentammines*,  $[\text{Co}(\text{NH}_3)_5(\text{OH})]\text{X}_2$ , or the **cobaltic roseo-salts**, include (1) Hydroxide ; (2) Chloride ; (3) Bromide ; (4) Iodide ; (5) Sulphate ; (6) Persulphate ; (7) Dithionate ; (8) Nitrate ; and (9) Trioxalatocobaltate.



- (ii) *Hydroxybispyridinetriammines*,  $[\text{Co}(\text{NH}_3)_3\text{py}_2(\text{HO})]\text{X}_2$ , represented by (1) Chloride; (2) Bromide; (3) Iodide; (4) Dithionate; (5) Nitrate; and (6) Thiocyanate.
- (iii) *Hydroxypyridinetetrammines*,  $[\text{Co}(\text{NH}_3)_4\text{py}(\text{HO})]\text{X}_2$ , represented by the Nitrate.
- (iv) *Hydroxyaquotetrammines*,  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{OH})]\text{X}_2$ , include (1) Chloride; (2) Bromide, and the double salt with iridium bromide; (3) Sulphate; (4) Bromosulphate, represented by a double salt with iridium; (5) Dithionate; (6) Selenate; (7) Nitrate; (8) 2 : 4 Dinitro- $\alpha$ -naphthyl-7-sulphonate; (9) Picrate; and (10) Dipicrylamide.
- (v) *Hydroxyaquobisethylenediamines*,  $[\text{Co en}_2(\text{H}_2\text{O})(\text{OH})]\text{X}_2$ , include cis- and trans-salts: (1) Chloride, and the double salt with iridium chloride; (2) Bromide; (3) Iodide; (4) Dithionate; (5) Nitrate; (6) Hydrophosphate; and (7) Thiocyanate.
- (vi) *Hydroxyaquobispyridinediammines*,  $[\text{Co}(\text{NH}_3)_2\text{py}_2(\text{H}_2\text{O})(\text{OH})]\text{X}_2$ , include (1) Chloride; (2) Bromide; (3) Dithionate; (4) Nitrate; and (5) Thiocyanate.
- (vii) *Fluopentammines*,  $[\text{Co}(\text{NH}_3)_5\text{F}]\text{X}_2$ , are represented by (1) Fluoride; (2) Chloride; (3) Nitrate; and (4) Chromate.
- (viii) *Fluobisethylenediamineammines*,  $[\text{Co}(\text{NH}_3)_2\text{en}_2\text{F}]\text{X}_2$ , include cis- and trans-salts: (1) Fluoride; (2) Perchlorate; (3) Bromide; (4) Dithionate; (5) Nitrate; and (6) Thiocyanate.
- (ix) *Chloropentammines*,  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{X}_2$ , are the **cobaltic chloropurpleo-salts**. They include (1) Hydroxide; (2) Chloride, and double salts with mercury, antimony, gold, iridium, and platinum chlorides; (3) Chlorite; (4) Chlorate; (5) Perchlorate; (6) Bromide, and double salts with the bromides of mercury, iridium, and platinum; (7) Iodide, the addition compounds with ammonia, and the double salts with mercury and bismuth iodides; (8) Polyiodide; (9) Sulphate; (10) Hydrosulphate; (11) Bromosulphate; (12) Iodosulphate; (13) Thiosulphate; (14) Dithionate; (15) Selenate; (16) Nitrate; (17) Carbonate; (18) Fluosilicate; (19) Pyrophosphate; (20) Hydro-pyrophosphate; (21) Chromate; (22) Dichromate; (23) Molybdate; (24) Hydrophosphatomolybdate; (25) Tungstates; (26) Tetra-isothiocyanatodiamminochromate; (27) Oxalate; (28) Hydro-tartrate; (29) Picrate; (30) Dipicrylamine; (31) 2 : 4 Dinitro- $\alpha$ -naphtholsulphonate; (32) 2 : 4-Dinitro- $\alpha$ -naphtholsulphonate; (33) Naphthalene- $\alpha$ -sulphonate, and other substituted benzene and naphthalenesulphonates.
- (x) *Chlorobisethylenediamineammines*,  $[\text{Co}(\text{NH}_3)_2\text{en}_2\text{Cl}]\text{X}_2$ , include cis- and trans-salts: (1) Chloride, and double salts with platinum; (2) Chloroperchlorate; (3) Bromide; (4) Chlorohydrosulphate; (5) Dithionate; (6) Nitrite; (7) Nitrate; (8) Dichromate; and (9) Bromocamphorsulphonate.
- (xi) *Chlorobisethylenediaminehydroxylamines*,  $[\text{Co}(\text{NH}_2\text{OH})\text{en}_2\text{Cl}]\text{X}_2$ , represented by (1) Chloride, and its double salts with gold and platinum chlorides; (2) Bromide; (3) Nitrate; and (4) Dichromate.
- (xii) *Bromobisethylenediaminehydroxylamines*,  $[\text{Co}(\text{NH}_2\text{OH})\text{en}_2\text{Br}]\text{X}_2$ , represented by (1) Chloride; (2) Bromide, and its double salt with platinum chloride; (3) Iodide; and (4) Nitrate.
- (xiii) *Chloroethylaminebisethylenediamines*,  $[\text{Co en}_2(\text{C}_2\text{H}_5\text{.NH}_2)\text{Cl}]\text{X}_2$ , include the chloride and iodide.
- (xiv) *Chloroallylaminebisethylenediamines*,  $[\text{Co en}_2(\text{C}_3\text{H}_5\text{.NH}_2)\text{Cl}]\text{X}_2$ , include cis- and trans-salts: (1) Chloride; (2) Bromide; (3) Iodide; (4) Dithionate; (5) Nitrate; and (6) Bromocamphorsulphonate.
- (xv) *Chloroanilinebisethylenediamines*,  $[\text{Co en}_2(\text{C}_6\text{H}_5\text{NH}_2)\text{Cl}]\text{X}_2$ , include (1)

- Chloride; (2) Bromide; (3) Iodide; (4) Chlorodithionate; (5) Nitrate; (6) Chloronitrate; (7) Bromocamphorsulphonate.
- (xvi) *Chloro-p-toluidinebisethylenediamines*,  $[\text{Co en}_2(\text{C}_7\text{H}_7\text{NH}_2\text{Cl})\text{X}_2]$ , include (1) Chloride; (2) Bromide; (3) Iodide; (4) Dithionate; and (5) Chloronitrate.
- (xvii) *Chlorobenzylaminebisethylenediamines*,  $[\text{Co en}_2(\text{C}_7\text{H}_7\text{NH}_2)\text{Cl}]\text{X}_2$ , include cis- and trans-salts: (1) Chloride; (2) Bromide; (3) Iodide; (4) Chlorodithionate; (5) Nitrate; and (6) Bromocamphorsulphonate.
- (xviii) *Chloropyridinebisethylenediamines*,  $[\text{Co en}_2\text{pyCl}]\text{X}_2$ , represented by (1) Chloride, and double salts with zinc, mercuric, stannous, and ferric chlorides; (2) Bromide; (3) Iodide; (4) Sulphate; (5) Nitrate; (6) Phosphate; and (7) Oxalate.
- (xix) *Chloroaquotetrammines*,  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{X}_2$ , include cis-salts: (1) Chloride, and double salts with mercury and platinum chlorides; (2) Bromide; (3) Sulphate; (4) Selenate; (5) Chloroselenate; (6) Nitrate; (7) Fluosilicate; and (8) Chromate.
- (xx) *Chloroaquobisethylenediamines*,  $[\text{Co en}_2(\text{H}_2\text{O})\text{Cl}]\text{X}_2$ , include some dextro- and lævo-salts: (1) Chloride; (2) Bromide; (3) Sulphate; (4) Dithionate; (5) Selenate; (6) Nitrate; (7) Bromonitrate; (8) Oxalate; and (9) Bromocamphorsulphonate.
- (xxi) *Chlorodiaquotriammines*,  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_2\text{Cl}]\text{X}_2$ , include (1) Chloride; (2) Bromide; (3) Sulphite—violet and grey; (4) Selenate; and (5) Nitrate.
- (xxii) *Chlorodiaquoethylenediamineammines*,  $[\text{Co}(\text{NH}_3)\text{en}(\text{H}_2\text{O})_2\text{Cl}]\text{X}_2$ , represented by the oxalate.
- (xxiii) *Chlorotriaquodiammines*,  $[\text{Co}(\text{NH}_3)_2(\text{H}_2\text{O})_3\text{Cl}]\text{X}_2$ , represented by the sulphate.
- (xxiv) *Bromopentammines*,  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{X}_2$ , or the **cobaltic bromopurpureo-salts**, include (1) Hydroxide; (2) Chloride, and double salts with the chlorides of mercury, and platinum; (3) Chlorate; (4) Perchlorate; (5) Bromide, and double salts with mercury, and platinum; (6) Iodide; (7) Sulphate; (8) Hydrosulphate; (9) Bromosulphate; (10) Iodosulphate; (11) Thiosulphate; (12) Dithionate; (13) Nitrate; (14) Fluosilicate; (15) Chromate; (16) Molybdate; (17) Tungstate; (18) Oxalate; (19) Picrate; and (20) Naphthalene- $\beta$ -sulphonate.
- (xxv) *Bromobisethylenediamineammines*,  $[\text{Co}(\text{NH}_3)\text{en}_2\text{Br}]\text{X}_2$ , include cis- and trans-salts, and some optically-active forms: (1) Chloride, and the double salt with platinum chloride; (2) Perchlorate; (3) Bromide; (4) Iodide; (5) Dithionate; (6) Nitrate; and (7) Bromocamphorsulphonate.
- (xxvi) *Bromohydroxylaminebisethylenediamines*,  $[\text{Co}(\text{NH}_2\text{OH})\text{en}_2\text{Br}]\text{X}_2$ , represented by (1) Hydroxide; (2) Chloride; (3) Bromide; (4) Iodide; (5) Dithionate; and (6) Nitrate.
- (xxvii) *Bromobisethylenediaminepyridines*,  $[\text{Co en}_2\text{pyBr}]\text{X}_2$ , represented by the bromide.
- (xxviii) *Bromoquotetrammines*,  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Br}]\text{X}_2$ , represented by the cis-salts: (1) Chloride; (2) Bromide; (3) Sulphate; (4) Bromosulphate; (5) Selenate; and (6) Nitrate.
- (xxix) *Bromoquobisethylenediamines*,  $[\text{Co en}_2(\text{H}_2\text{O})\text{Br}]\text{X}_2$ , represented by the cis-salts: (1) Bromide; (2) Nitrite; and (3) Nitrate.
- (xxx) *Iodopentammines*,  $[\text{Co}(\text{NH}_3)_5\text{I}]\text{X}_2$ , include (1) Chloride; (2) Chlorate; (3) Bromide; (4) Iodide; (5) Sulphate; (6) Nitrate; (7) Picrate; and (8) Dichromate.
- (xxxi) *Nitrosopentammines*,  $[\text{Co}(\text{NH}_3)_5(\text{NO})]\text{X}_2$ , include (1) Chloride; (2) Iodate; (3) Sulphate; and (4) Nitrate.

- (xxxii) *Dinitrosopentammines*,  $[\text{Co}_2(\text{NH}_3)_{10}(\text{N}_2\text{O}_2)]\text{X}_4$ , include (1) Chloride; (2) Hydroperchlorate; (3) Bromide; (4) Hydrobromide; (5) Iodide; (6) Hydrobromide; (7) Iodide; (8) Hydroiodate; (9) Sulphate; (10) Hydrosulphate; (11) Nitrate; (12) Hydrionitrate; (13) Iodonitrate; (14) Oxalate; (15) Hydroxalate; and (16) Chromate.
- (xxxiii) *Nitropentammines*,  $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{X}_2$ . These salts were designated **cobaltic xantho-salts**—from *ξανθός*, yellow—by O. W. Gibbs and F. A. Genth, in allusion to their colour. They include (1) Chloride, and double salts with gold, mercury, and platinum chlorides; (2) Chlorate; (3) Perchlorate; (4) Bromide; (5) Iodide; (6) Sulphate; (7) Hydrosulphate; (8) Iodosulphate; (9) Thiosulphate; (10) Selenate; (11) Nitrite; (12) Hexanitrocobaltate; (13) Tetranitrodiamminocobaltate; (14) Nitrate; (15) Chloronitrate; (16) Bromonitrate; (17) Sulphatonitrate; (18) Amidosulphonate; (19) Imidosulphonate; (20) Hydroxylaminedisulphonate; (21) Hydroxylamineiso-disulphonate; (22) Fluosilicate; (23) Chromate; (24) Dichromate; (25) Molybdate; (26) Tungstate; (27) Oxalate; (28) Picrate; (29) Hexacyanoferroate; and (30) Tetraisothiocyanatodiamminochromate.
- (xxxiv) *Nitritopentammines*,  $[\text{Co}(\text{NH}_3)_5(\text{ONO})]\text{X}_2$ , the **cobaltic isoxantho-salts** of S. M. Jörgensen, and represented by the chloride.
- (xxxv) *Nitritobisethylenediamineammines*,  $[\text{Co}(\text{NH}_3)_2\text{en}_2(\text{NO}_2)]\text{X}_2$ , include cis- and trans-salts: (1) Chloride; (2) Bromide; (3) Iodide; (4) Sulphate; (5) Dithionate; (6) Nitrite; (7) Nitrate; (8) Bromonitrate; (9) Thiocyanate; and (10) Bromocamphorsulphonate.
- (xxxvi) *Hydroxyaquotetrammines*,  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{OH})]\text{X}_2$ , represented by the hydroxide, and by complexes with the picrate, 2:4-dinitro- $\alpha$ -naphthoxide-7-sulphonate, and picrylamide.
- (xxxvii) *Nitritoaquotetrammines*,  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{NO}_2)]\text{X}_2$ , include (1) Hydroxide; (2) Chloride, and double salts with gold, iridium, and platinum chlorides; (3) Bromide and a double salt with iridium bromide; (4) Iodide; (5) Sulphate; (6) Hydrosulphate; (7) Selenate; (8) Hydroselenate; (9) Nitrate; (10) Tetranitrodiamminocobaltate; (11) Carbonate; (12) Oxalate; and (13) Tartrate.
- (xxxviii) *Nitritopyridinetriammines*,  $[\text{Co}(\text{NH}_3)_3\text{py}_2(\text{NO}_2)]\text{X}_2$ , represented by (1) Bromide; (2) Dithionate; and (3) Nitrite.
- (xxxix) *Nitritoaquobisethylenediamines*,  $[\text{Co en}_2(\text{H}_2\text{O})(\text{NO}_2)]\text{X}_2$ , include cis- and trans-salts: (1) Chloride; and (2) Sulphate.
- (xl) *Nitritoaquobis trimethylenediamines*,  $[\text{Co tr}_2(\text{H}_2\text{O})(\text{NO}_2)]\text{X}_2$ , represented by the (1) Bromide; (2) Nitrate; and (3) Thiocyanate.
- (xli) *Dinitritodiaminopentanes*,  $[\text{Co ptn}_2(\text{NO}_2)_2]\text{X}$ , represented by the nitrate of the  $\alpha$ - and  $\beta$ - $\beta\delta$ -diaminopentanes.
- (xlii) *Nitratopentammines*,  $[\text{Co}(\text{NH}_3)_5(\text{NO}_3)]\text{X}_2$ , are the **cobaltic purpureo-salts**—from *purpura*, purple—of E. Frémy, and now also called **cobaltic nitratopurpureo-salts**. They include (1) Chloride, and the double salts with the chlorides of mercury and platinum; (2) Chlorate; (3) Perchlorate; (4) Bromide; (5) Iodide; (6) Sulphate; (7) Dithionate; (8) Selenate; (9) Nitrate; (10) Hexanitrocobaltate; (11) Tetranitrodiamminocobaltate; (12) Carbonate; (13) Fluosilicate; (14) Chromate; (15) Dichromate; (16) Molybdate; (17) Tungstate; (18) Oxalate; (19) Picrate; and (20) Naphthalene- $\beta$ -sulphonate.
- (xliii) *Nitratobisethylenediaminammines*,  $[\text{Co}(\text{NH}_3)_2\text{en}_2(\text{NO}_3)]\text{X}_2$ , include cis- and trans-salts: (1) Bromide; (2) Dithionate; and (3) Nitrate.
- (xliv) *Nitratoaquotetrammines*,  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{NO}_3)]\text{X}_2$ , are represented by the nitrate.

- (xlv) *Metaboratopentammines*,  $[\text{Co}(\text{NH}_3)_5(\text{BO}_2)]\text{X}_2$ , represented by the chloride.
- (xlvi) *Hydrocarbonatopentammines*,  $[\text{Co}(\text{NH}_3)_5(\text{HCO}_3)]\text{X}_2$ , represented by (1) Bromide; (2) Polyiodide; (3) Dithionate; and (4) Nitrate.
- (xlvii) *Cyanoaquotetrammines*,  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cy}]\text{X}_2$ , represented by the chloride.
- (xlviii) *Isothiocyanatopentammines*,  $[\text{Co}(\text{NH}_3)_5(\text{SCy})]\text{X}_2$ , represented by (1) Chloride, and double salts with platinum chlorides; (2) Bromide; (3) Iodide; (4) Sulphate; (5) Selenate; (6) Nitrite; (7) Nitrate; (8) Thiocyanate; (9) Chromate; (10) Molybdate; and (11) Tungstate.
- (xlix) *Isothiocyanatobisethylenediamineammines*,  $[\text{Co}(\text{NH}_3)\text{en}_2(\text{SCy})]\text{X}_2$ , include cis- and trans-salts, and dextro- and lævo-salts: (1) Chloride; (2) Perchlorate; (3) Bromide; (4) Iodide; (5) Dithionate; (6) Bromodithionate; (7) Nitrite; (8) Nitrate; (9) Thiocyanate; and (10) Chlorodithionate.
  - (l) *Isothiocyanatoaquotetrammines*,  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{SCy})]\text{X}_2$ , include (1) Chloride; (2) Bromide; (3) Nitrite; and (4) Nitrate.
  - (li) *Isothiocyanatoaquobisethylenediamines*,  $[\text{Co en}_2(\text{H}_2\text{O})(\text{SCy})]\text{X}_2$ , include cis- and trans-salts: (1) Perchlorate; (2) Bromide; (3) Dithionate; (4) Nitrite; (5) Nitrate; and (6) Thiocyanate.
  - (lii) *Acetatopentammines*,  $[\text{Co}(\text{NH}_3)_5(\text{C}_2\text{H}_3\text{O}_2)]\text{X}_2$ , include (1) Chloride, represented by a double salt with platinous chloride; (2) Iodide; and (3) Nitrate.
  - (liii) *Propionatopentammines*,  $[\text{Co}(\text{NH}_3)_5(\text{C}_3\text{H}_5\text{O}_2)]\text{X}_2$ , represented by the nitrate.
  - (liv) *p-Nitrophenolatoquobisethylenediamines*,  $[\text{Co en}_2(\text{H}_2\text{O})(p\text{-C}_6\text{H}_4\text{O}_3\text{N})]\text{X}_2$ , represented by the mono-, di-, and tri-hydrates of the *p*-nitrophenolates, and addition compounds with *p*-nitrophenol.
  - (lv) *Bis-p-Nitrophenolatobisethylenediamines*,  $[\text{Co en}_2(p\text{-C}_6\text{H}_5\text{O}_3\text{N-acid})(p\text{-C}_6\text{H}_4\text{O}_3\text{N})]\text{X}_2$ , represented by the *p*-nitrophenolate.
  - (lvi) *Bis-o-nitrophenolatobisethylenediamines*,  $[\text{Co en}_2(o\text{-C}_6\text{H}_5\text{O}_3\text{N-acid})(o\text{-C}_6\text{H}_4\text{O}_3\text{N})]\text{X}_2$ , represented by the *o*-nitrophenolate.
  - (lvii) *Dinitrophenolatoquobisethylenediamines*,  $[\text{Co en}_2(\text{C}_6\text{H}_3\text{O}_5\text{N}_2)]\text{X}_2$ , represented by the 2: 4- and the 2: 6-dinitrophenolates, and a basic salt.
  - (lviii) *Picratopentammines*,  $[\text{Co}(\text{NH}_3)_5(\text{C}_2\text{H}_2\text{O}_7\text{N}_3)]\text{X}_2$ , represented by the picrate, and a basic salt.
  - (lix) *Picratoquobisethylenediamines*,  $[\text{Co en}_2(\text{H}_2\text{O})(\text{C}_6\text{H}_2\text{O}_7\text{N}_3)]\text{X}_2$ , represented by the picrate.
  - (lx) *Glycinebisethylenediamines*,  $[\text{Co en}_2(\text{C}_2\text{H}_4\text{O}_2\text{N})]\text{X}_2$ , in which the univalent radicle in the inner complex has a principal and a secondary valency, and represented by some optically-active salts: (1) Chloride, (2) Iodide; (3) Dithionate; and (4) Bromocamphorsulphonate.
  - (lxi) *Sarcosinebisethylenediamines*,  $[\text{Co en}_2(\text{C}_3\text{H}_6\text{O}_2\text{N})]\text{X}_2$ , represented by the (1) Chloride; (2) Iodide; (3) Dithionate; and (4) Bromocamphorsulphonate.
  - (lxii) *Acetylacetonatobisethylenediamines*,  $[\text{Co en}_2(\text{C}_5\text{H}_7\text{O}_2)]\text{X}_2$ , represented by some optically-active salts: (1) Chloride; (2) Perchlorate; (3) Bromide; (4) Iodide; (5) Sulphate; (6) Persulphate; (7) Nitrate; and (8) Thiocyanate.
  - (lxiii) *Propionylacetonatobisethylenediamines*,  $[\text{Co en}_2(\text{COH}_5\text{O}_2)]\text{X}_2$ , represented by some optically-active salts: (1) Chloride; (2) Perchlorate; (3) Bromide; (4) Iodide; (5) Sulphate; (6) Persulphate; (7) Nitrate; and (8) Thiocyanate.
  - (lxiv) *Pæonolobisethylenediamines*,  $[\text{Co en}_2(\text{C}_9\text{H}_9\text{O}_3)]\text{X}_2$ , represented by (1) Chlorate; (2) Perchlorate; (3) Bromide; (4) Iodide; (5) Dithionate; (6) *d*- and *l*-tartrate.

(lxv) *Benzhydroxamatobisethylenediamines*,  $[\text{Co en}_2(\text{C}_7\text{H}_6\text{O}_2\text{N})]\text{X}_2$ , represented by (1) Perchlorate; (2) Bromide; (3) Sulphate; (4) Dithionate; and (5) Thiocyanate.

(lxvi)  *$\alpha$ -Benzilmonoximebisdiethylenediamine*,  $[\text{Co en}_2(\text{C}_{14}\text{H}_{10}\text{O}_2\text{N})]\text{X}_2$ , represented by (1) Bromide; and (2) Iodide.

(b) *Pentammines with a Bivalent Radicle in Complex.*

(lxvii) *Sulphitopentammines*,  $[\text{Co}(\text{NH}_3)_5(\text{SO}_3)]\text{X}$ , represented by (1) Chloride; (2) Hydrochloride; (3) Bromide; (4) Sulphite, and double salts with sodium sulphite; (5) Thiosulphate; and (6) Nitrate.

(lxviii) *Sulphitoaquotetrammines*,  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{SO}_3)]\text{X}$ , represented by (1) Hydroxide; (2) Sulphite; (3) Cyanide; and (4) Thiocyanate.

(lxix) *Sulphatopentammines*,  $[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]\text{X}$ , or **cobaltic sulphato-purpureo-salts**, include (1) Chloride, and the double salt with platinum chloride; (2) Chlorate; (3) Perchlorate; (4) Bromide, and the double salt with iridium bromide; (5) Iodide; (6) Sulphate; (7) Hydrosulphate; (8) Selenate; (9) Nitrate; (10) Carbonate; (11) Fluosilicate; (12) Chromate; (13) Dichromate; and (14) Picrate.

(lxx) *Sulphatoaquotetrammines*,  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{SO}_4)]\text{X}$ , include (1) Chloride; (2) Perchlorate; (3) Bromide; (4) Iodide; (5) Sulphate; (6) Hydrosulphate; (7) Selenate; and (8) Nitrate.

(lxxi) *Sulphatodiaquotriammines*,  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_2(\text{SO}_4)]\text{X}$ , represented by the sulphate.

(lxxii) *Thiosulphatopentammines*,  $[\text{Co}(\text{NH}_3)_5(\text{S}_2\text{O}_3)]\text{X}$ , include (1) Chloride; (2) Bromide; (3) Iodide; (4) Thiosulphate; (5) Dithionate; (6) Chromate; and (7) Nitrate.

(lxxiii) *Selenitopentammines*,  $[\text{Co}(\text{NH}_3)_5(\text{SeO}_3)]\text{X}$ , include (1) Chloride; and (2) Selenite.

(lxxiv) *Selenatopentammines*,  $[\text{Co}(\text{NH}_3)_5(\text{SeO}_4)]\text{X}$ , include (1) Chloride, represented by the double salt with platinum chloride; (2) Bromide; (3) Sulphate; (4) Selenate; (5) Hydroselenate; and (6) Nitrate.

(lxxv) *Selenatoaquotetrammines*,  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{SeO}_4)]\text{X}$ , represented by the (1) Chloride; and (2) Sulphate.

(lxxvi) *Carbonatopentammines*,  $[\text{Co}(\text{NH}_3)_5(\text{CO}_3)]\text{X}$ , include (1) Chloride; (2) Bromide; (3) Iodide; (4) Selenate; (5) Nitrate; (6) Oxalate; and (7) Tungstate.

(lxxvii) *Oxalatopentammines*,  $[\text{Co}(\text{NH}_3)_5(\text{C}_2\text{O}_4)]\text{X}$ , include (1) Chloride, represented by the double salt with platinum chloride; (2) Hydrochloride; (3) Bromide; (4) Hydrobromide; (5) Iodide; (6) Hydroiodide; (7) Sulphate; (8) Hydrosulphate; (9) Selenate; (10) Hydroselenate; (11) Nitrate; (12) Hydronitrate; (13) Oxalate; (14) Hydroxalate; and (15) Trioxalatocobaltate.

(lxxviii) *Sulphoacetatopentammines*,  $[\text{Co}(\text{NH}_3)_5(\text{C}_2\text{H}_3\text{O}_5\text{S})]\text{X}$ , represented by the nitrate.

(lxxix) *Mesotartratopentammines*,  $[\text{Co}(\text{NH}_3)_5(\text{C}_4\text{H}_4\text{O}_6)]\text{X}$ , represented by the nitrate.

(lxxx) *Maleatopentammines*,  $[\text{Co}(\text{NH}_3)_5(\text{C}_4\text{H}_2\text{O}_4)]\text{X}$ , represented by the nitrate.

(lxxxi) *Phthalatopentammines*,  $[(\text{Co}(\text{NH}_3)_5(\text{C}_8\text{H}_4\text{O}_4)]\text{X}$ , represented by the nitrate.

(lxxxii) *Hydrophosphatopentammines*,  $[\text{Co}(\text{NH}_3)_5(\text{HPO}_4)]\text{X}$ , represented by the hydrophosphate.

(lxxxiii) *Chromatopentammines*,  $[\text{Co}(\text{NH}_3)_5(\text{CrO}_4)]\text{X}$ , include (1) Chloride; (2) Chromate; and (3) Nitrate.

(lxxxiv) *Carbonatobispentammines*,  $[\{\text{Co}(\text{NH}_3)_5\}_2(\text{CO}_3)]\text{X}_4$ , represented by the sulphate.

- (lxxxv) *Malonatobispentammines*,  $[\{\text{Co}(\text{NH}_3)_5\}_2(\text{C}_3\text{H}_2\text{O}_4)]\text{X}_4$ , represented by (1) Nitrate; and (2) Nitratomalonate.
- (lxxxvi) *Glutaratobispentammines*,  $[\{\text{Co}(\text{NH}_3)_5\}_2(\text{C}_5\text{H}_6\text{O}_4)]\text{X}_4$ , represented by (1) Nitrate; and (2) Nitratoglutarate.
- (lxxxvii) *Adipinatobispentammines*,  $[\{\text{Co}(\text{NH}_3)_5\}_2(\text{C}_6\text{H}_8\text{O}_4)]\text{X}_4$ , represented by the nitrate.
- (lxxxviii) *Malatobispentammines*,  $[\{\text{Co}(\text{NH}_3)_5\}_2(\text{C}_4\text{H}_4\text{O}_5)]\text{X}_4$ , represented by (1) Nitrate; and (2) Nitratomalate.
- (lxxxix) *Mesolatratobispentammines*,  $[\text{Co}\{(\text{NH}_3)_5\}_2(\text{C}_4\text{H}_4\text{O}_6)]\text{X}_4$ , represented by the nitratomesotartrate.
- (xc) *Maleatobispentammines*,  $[\{\text{Co}(\text{NH}_3)_5\}_2(\text{C}_3\text{H}_2\text{O}_4)]\text{X}_4$ , represented by the nitrate.
- (xci) *Citraconatobispentammines*,  $[\{\text{Co}(\text{NH}_3)_5\}_2(\text{C}_5\text{H}_4\text{O}_4)]\text{X}_4$ , represented by (1) Nitrate, and (2) Nitratoitaconate.
- (xcii) *Itaconatobispentammines*,  $[\{\text{Co}(\text{NH}_3)_5\}_2(\text{C}_5\text{H}_4\text{O}_4)]\text{X}_4$ , represented by (1) Nitrate; and (2) Nitratoitaconate.
- (xciii) *Phthalatobispentammines*,  $[\{\text{Co}(\text{NH}_3)_5\}_2(\text{C}_8\text{H}_4\text{O}_2)]\text{X}_4$ , represented by the nitrate.
- (xciv) *Methionatobispentammines*,  $[\{\text{Co}(\text{NH}_3)_5\}_2(\text{CH}_2\text{O}_6\text{S}_2)]\text{X}_4$ , represented by the nitratomethionate.
- (xcv) *Bisdimethylglyoximediamines* including (1) Chloride; (2) Bromide; (3) Iodide; (4) Sulphate; and (5) Thiocyanate.
- (c) *Pentammines with a Tervalent Radicle in Complex.*
- (xcvi) Represented by (1) *Phosphatopentammines*,  $[\text{Co}(\text{NH}_3)_5(\text{PO}_4)]2\text{H}_2\text{O}$ ; (2) *Citratopentamine*,  $[\text{Co}(\text{NH}_3)_5(\text{C}_6\text{H}_5\text{O}_7)]2\text{H}_2\text{O}$ ; and (3) *Hexacyanoferripentamine*,  $[\text{Co}(\text{NH}_3)_5(\text{Fe}'''\text{Cy}_6)]$ .
- (xcvii) *Hydrocitratotripentammines*,  $[\{\text{Co}(\text{NH}_3)_5\}_3(\text{C}_6\text{H}_5\text{O}_7)'''](\text{C}_6\text{H}_7\text{O}_7)'$ .
- (d) *Pentammines with a Polyvalent Acidic Radicle in Complex.*
- (xcviii) With a quadrivalent radicle represented by (1) *Pyrophosphatopentammines*,  $\text{Na}[\text{Co}(\text{NH}_3)_5(\text{P}_2\text{O}_7)]$ ; and (2) *Hexacyanoferroropentammines*,  $\text{K}[\text{Co}(\text{NH}_3)_5(\text{Fe}'''\text{Cy}_6)]$ .
- (xcix) With quinequevalent radicle represented by *benzopentacarbonatopentammines*,  $\text{Na}_2[\text{Co}(\text{NH}_3)_5\{\text{C}_6\text{H}(\text{CO}_2)_5\}]$ .
- (c) With a sexivalent radicle represented by *benzolhexacarbonatopentammines*,  $\text{Na}_3[\text{Co}(\text{NH}_3)_5\{\text{C}_6(\text{CO}_2)_6\}]$ .

### III.—The Tetrammine family, or compounds of the univalent group: $[\text{CoA}_4\text{X}_2]'$ .

- (i) *Dihydroxytetrammines*,  $[\text{Co}(\text{NH}_3)_4(\text{OH})_2]\text{X}$ , represented by the hydroxide and by complexes with the picrate, and picrylamide.
- (ii) *Difluotetrammines*,  $[\text{Co}(\text{NH}_3)_4\text{F}_2]\text{X}$ , represented by the chloride.
- (iii) *Difluobisethylenediamines*,  $[\text{Co en}_2\text{F}_2]\text{X}$ , represented by cis- and trans-salts: (1) Fluoride; (2) Chloride; (3) Perchlorate; (4) Bromide; (5) Iodide; (6) Dithionate; and (7) Thiocyanate.
- (iv) *Dichlorotetrammines*,  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{X}$ , represented by the cis-salts, or **cobaltic violeo-salts**, named by A. Werner—from *viola*, a violet—in allusion to the colour; and trans-salts, or **cobaltic praseo-salts**, named by O. W. Gibbs and F. A. Genth—from *πρασῖος*, leek-green—in allusion to the colour. (1) Fluoride; (2) Chloride, and double salts with mercury, gold, platinum, and iridium chlorides; (3) Chlorate; (4) Bromide; (5) Iodide; (6) Sulphate; (7) Hydro-sulphate, and double salts with silver, and bismuth sulphates; (8) Dithionate; (9) Hydroselenate; (10) Nitrite; (11) Nitrate; (12) Dichromate; (13) Picrate; (14) Thiocyanate; (15) Hexacyanochromate; and (16) Hexacyanoferrate.

- (v) *Dichloroquaterpyridine*,  $[\text{Co py}_4\text{Cl}_2]\text{X}$ , represented by the trans-salts : (1) Chloride, and its double salts with the chlorides of mercury, gold, and platinum ; (2) Bromide ; (3) Hydrosulphate ; (4) Dithionate ; (5) Benzylthiosulphate ; (6) Hydroselenate ; (7) Nitrate ; and (8) Tetranitrodiamminocobaltate.
- (vi) *Dichlorobisethylenediamines*,  $[\text{Co en}_2\text{Cl}_2]\text{X}$ , represented by cis- or **violet**-salts, and trans- or **praseo**-salts, as well as by optically-active forms : (1) Hydroxide ; (2) Chloride, as well as ammonia addition compounds, and double salts with the chlorides of copper, cadmium, mercury, stannous and stannic tin, bismuth, antimony, iridium, and platinum ; (3) Hydrochloride ; (4) Bromide, and a double salt with cadmium bromide ; (5) Iodide, and a double salt with cadmium, and mercury iodides ; (6) Sulphate ; (7) Hydrosulphate ; (8) Dithionate ; (9) Nitrite ; (10) Nitrate ; (11) Thiocyanate ; (12) Monochloroacetate ; (13) Dichloroacetate ; (14) Dibromoacetate ; (15) Oxalate ; (16) Malonate ; (17) Methylmalonate ; (18) Ethylmalonate ; (19) Chloromalonate ; (20) Bromomalonate ; (21) Succinate ; (22) Dibromosuccinate ; (23) Glutarate ; (24) Adipate ; (25) Tartrate ; (26) Mesotartrate ; (27) Malleate ; (28) Fumarate ; (29) Citraconate ; (30) Mesaconate ; (31) Itaconate ; (32) Acetodicarbonate ; (33) Phthalate ; (34) Thiodiacetate ; (35) Dithiodiacetate ; (36) Dithiodilactate ; (37) Thiodilactate ; (38) Sulphonyldiacetate ; (39) Sulphoacetate ; (40) Sulphobenzoate ; (41) Benzylsulphoacetate ; and (42) Methionate.
- (vii) *Dichlorobispropylenediamines*,  $[\text{Co pn}_2\text{Cl}_2]\text{X}$ , include cis- and trans-salts : (1) Chloride, and double salts with mercury, gold, and platinum chlorides ; (2) Hydrochloride ; (3) Bromide ; (4) Sulphate ; (5) Hydrosulphate ; (6) Dithionate ; (7) Nitrate ; (8) Permanganate ; (9) Thiocyanate ; and (10) Hexacyanoferrate.
- (viii) *Dichlorobistrimethylenediamines*,  $[\text{Co}\{\text{NH}_2(\text{CH}_2)_3\text{NH}_2\}_2\text{Cl}_2]\text{X}$ , is represented by the trans-chloride, and its double salt with platinum chloride.
- (ix) *Dichlorobiscyclopentanediamines*,  $[\text{Co}(\text{C}_5\text{H}_{12}\text{N}_2)_2\text{Cl}_2]\text{X}$ , are represented by the cis- and trans-chloride.
- (x) *Dichlorobispyridinediammines*,  $[\text{Co}(\text{NH}_3)_2\text{py}_2\text{Cl}_2]\text{X}$ , are represented by (1) Chloride ; and (2) Nitrate.
- (xi) *Dichlorobisethylenediaminediammines*,  $[\text{Co}(\text{NH}_3)_2\text{en}_2\text{Cl}_2]\text{X}$ , is represented by cis- and trans-salts : (1) Chloride ; (2) Bromide ; (3) Iodide ; (4) Hydrosulphate ; (5) Dithionate ; (6) Nitrate ; and (7) Thiocyanate.
- (xii) *Dichlorodiaminopentanes*,  $[\text{Co ptn}_2\text{Cl}_2]\text{X}$ , represented by the chloride of  $\alpha\beta\delta$ - and  $\beta\beta\delta$ -diaminopentanes.
- (xiii) *Dichloroaquotriammines*,  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})\text{Cl}_2]\text{X}$ , were called by F. Rose, **cobaltic dichro-salts**—from  $\delta\acute{\iota}\chi\rho\omega\mu\omicron\varsigma$ , two-coloured—in allusion to the dichroism of the salts. The series include (1) Chloride—grey, and greyish-green forms ; (2) Sulphate ; (3) Hydrosulphate ; (4) Nitrate ; and (5) Tetranitrodiamminocobaltate.
- (xiv) *Dichloroaquoethylenediamineammines*,  $[\text{Co}(\text{NH}_3)\text{en}(\text{H}_2\text{O})\text{Cl}_2]\text{X}$ , represented by the trans-salts : (1) Chloride ; and (2) Nitrate.
- (xv) *Dichlorodiaquodiammines*,  $[\text{Co}(\text{NH}_3)_2(\text{H}_2\text{O})_2\text{Cl}_2]\text{X}$ , include (1) Chloride—green, and blue forms ; (2) Hydrosulphate ; (3) Hydroselenate ; and (4) Nitrate.
- (xvi) *Dibromotetrammines*,  $[\text{Co}(\text{NH}_3)_4\text{Br}_2]\text{X}$ , include the trans- or praseo-salts : (1) Chloride, and its double salt with platinum chloride ; (2) Bromide, and its double salts with mercury and platinum bromides ; (3) Hydrobromide ; (4) Iodide ; (5) Dithionate ; (6) Nitrate ; (7) Thiocyanate ; and (8) Hydrothiodiacetate.

- (xvii) *Dibromobis(trimethylenediamines)*,  $[\text{Co tr}_2\text{Br}_2]\text{X}$ , represented by the bromide.
- (xviii) *Dibromo-aquobis(ethylenediamine)ammines*,  $[\text{Co}(\text{NH}_3)\text{en}(\text{H}_2\text{O})\text{Br}_2]\text{X}$ , represented by the bromide.
- (xix) *Dihydroselenatotetrammines*,  $[\text{Co}(\text{NH}_3)_4(\text{HSeO}_4)_2]\text{X}$ , represented by the selenate.
- (xx) *Dinitrotetrammines*,  $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]\text{X}$ , S. M. Jørgensen named the cis-salts the **cobaltic flavo-salts**—from *flavus*, yellow—in allusion to the colour. O. W. Gibbs called the trans-salts—**cobaltic croceo-salts**—from *croceus*, saffron-red—in allusion to the colour: (1) Hydroxide; (2) Chloride, and double salts with the chlorides of gold, cadmium, mercury, platinum, and iridium; (3) Chlorate; (4) Perchlorate; (5) Bromide, with its ammonia addition compounds, and double salts with cadmium, mercury, and iridium bromides; (6) Iodide, and double salts with mercury, and bismuth iodides; (7) Polyiodide; (8) Sulphate; (9) Selenate; (10) Nitrite; (11) Nitrate, and double salts with potassium, and rubidium nitrates; (12) Hydronitrate; (13) Hexanitrocobaltate; (14) Tetranitrodiammincobaltate; (14) Amidosulphonate; (15) Hydroxylaminesulphonate; (16) Fluosilicate; (17) Chromate; (18) Dichromate; (19) Molybdate; (20) Tetraisothiocyanatodiammincobaltate; (21) Picrate; and (22) Naphthalene- $\beta$ -sulphonate.
- (xxi) *Dinitrobis(ethylenediamines)*,  $[\text{Co en}_2(\text{NO}_2)_2]\text{X}$ , include cis- or flavo-salts, and trans- or croceo-salts, as well as optically-active forms: (1) Hydroxide; (2) Chloride, and double salts with the chlorides of platinum; (3) Perchlorate; (4) Bromide; (5) Iodide; (6) Sulphate; (7) Hydrosulphate; (8) Nitrite; (9) Nitrate; (10) Thiocyanate; (11) Camphorsulphonate; and (12) Bromocamphorsulphonate.
- (xxii) *Dinitrobis(trimethylenediamines)*,  $[\text{Co}\{\text{NH}_2(\text{CH}_2)_3\text{NH}_2\}_2(\text{NO}_2)_2]\text{X}$ , with the trans-salts: (1) Chloride; (2) Bromide; (3) Iodide; (4) Nitrite; and (5) Nitrate.
- (xxiii) *Dinitrobis(pyridinediammines)*,  $[\text{Co}(\text{NH}_3)_2\text{py}_2(\text{NO}_2)_2]\text{X}$ , and the trans-salts: (1) Bromide; (2) Dithionate; and (3) Nitrate.
- (xxiv) *Dinitropropylenediaminethylenediamines*,  $[\text{Co en pn}(\text{NO}_2)_2]\text{X}$ , represented by cis- or flavo-salts, and trans- or croceo-salts, as well as by active forms: (1) Chloride; (2) Bromide; (3) Sulphate; (4) Nitrite; (5) Thiocyanate; and (6) Bromocamphorsulphonate.
- (xxv) *Dinitro-aquotriammines*,  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})(\text{NO}_2)_2]\text{X}$ , represented by the hydroxide.
- (xxvi) *Dinitrobis(ethylenediamines)*,  $[\text{Co en}_2(\text{ONO})_2]\text{X}$ , represented by cis- and trans-salts: (1) Chloride; (2) Bromide; (3) Iodide; (4) Dithionate; (5) Nitrate; and (6) Thiocyanate.
- (xxvii) *Dinitrobis(pyridinediammines)*,  $[\text{Co}(\text{NH}_3)_2\text{py}_2(\text{ONO})_2]\text{X}$ , represented by the trans-salts: (1) Bromide; (2) Iodide; (3) Dithionate; (4) Iodide; (5) Nitrate; and (6) Dithionate.
- (xxviii) *Dinitratotetrammines*,  $[\text{Co}(\text{NH}_3)_4(\text{NO}_3)_2]\text{X}$ , represented by the nitrate.
- (xxix) *Dinitratobis(ethylenediamines)*,  $[\text{Co en}_2(\text{NO}_3)_2]\text{X}$ , represented by (1) Bromide; (2) Nitrate; and (3) Hydronitrate.
- (xxx) *Nitratonitrobis(trimethylenediamine)*,  $[\text{Co tr}_2(\text{NO}_2)(\text{NO}_3)]\text{X}$ , represented by the nitrate.
- (xxxi) *Bissalicylatobis(ethylenediamines)*,  $[\text{Co en}_2(\text{C}_7\text{H}_5\text{O}_3)_2]\text{X}$ , represented by the salicylate.
- (xxxii) *Bisnitrophenolatobis(ethylenediamines)*,  $[\text{Co en}_2(\text{C}_6\text{H}_4\text{O}_3\text{N})_2]\text{X}$ , represented by the *m*- and *p*-nitrophenolates, and a double salt with sodium *m*-nitrophenolate.



- (xxxiii) *Dithiocyanatotetrammines*,  $[\text{Co}(\text{NH}_3)_4(\text{SCy})_2]\text{X}$ , represented by the iodide.
- (xxxiv) *Dithiocyanatotriaminotriethylamine*,  $[\text{Co}(\text{NH}_3)_3\{(\text{C}_2\text{H}_5)_3\text{N}\}(\text{SCy})_2]\text{X}$ , represented by (1) Chloride, and its double salt with platinum; (2) Nitrate; and (3) Thiocyanate.
- (xxxv) *Diisothiocyanatobisethylenediamines*,  $[\text{Co en}_2(\text{SCy})_2]\text{X}$ , includes cis- and trans-salts: (1) Chloride; (2) Bromide; (3) Iodide; (4) Sulphate; (5) Hydrosulphate; (6) Dithionate; (7) Hydroselenate; (8) Nitrate; and (9) Thiocyanate.
- (xxxvi) *Diisothiocyanatobispropylenediamines*,  $[\text{Co pn}_2(\text{SCy})_2]\text{X}$ , include (1) Chloride; (2) Bromide; (3) Iodide; and (4) Thiocyanate.
- (xxxvii) *Nitrohydroxytetrammines*,  $[\text{Co}(\text{NH}_3)_4(\text{OH})(\text{NO}_2)]\text{X}$ , include (1) Chloride; (2) Bromide; (3) Iodide; and (4) Nitrate.
- (xxxviii) *Nitratonitrobisethylenediamines*,  $[\text{Co en}_2(\text{NO}_2)(\text{NO}_3)]\text{X}$ , represented by the trans-nitrate, and hydronitrate.
- (xxxix) *Fluohydroxytetrammines*,  $[\text{Co}(\text{NH}_3)_4(\text{OH})\text{F}]\text{X}$ , represented by the nitrate.
- (xl) *Chlorohydroxytetrammines*,  $[\text{Co}(\text{NH}_3)_4(\text{OH})\text{Cl}]\text{X}$ , represented by the dithionate.
- (xli) *Chlorohydroxybisethylenediamines*,  $[\text{Co en}_2(\text{OH})\text{Cl}]\text{X}$ , include cis- and trans-salts, and optically-active salts: (1) Chloride; (2) Bromide; and (3) Nitrate.
- (xlii) *Chloronitrotetrammines*,  $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)\text{Cl}]\text{X}$ , include (1) Chloride; (2) Bromide; (3) Iodide; (4) Nitrate; (5) Dichlorodinitrodiamminocobaltate; and (6) Thiocyanate.
- (xliii) *Chloronitrobisethylenediamines*,  $[\text{Co en}_2(\text{NO}_2)\text{Cl}]\text{X}$ , include cis- and trans-salts, as well as optically-active salts: (1) Chloride; (2) Bromide; (3) Iodide; (4) Hydrosulphate; (5) Nitrite; (6) Nitrate; (7) Hydronitrate; (8) Thiocyanate; (9) Camphorsulphonate; and (10) Bromocamphorsulphonate.
- (xliv) *Chloronitrobispyridinediammines*,  $[\text{Co}(\text{NH}_3)_2\text{py}_2(\text{NO}_2)\text{Cl}]\text{X}$ , represented by the nitrate.
- (xlv) *Bromohydroxybisethylenediamines*,  $[\text{Co en}_2(\text{OH})\text{Br}]\text{X}$ , represented by the bromide.
- (xlvi) *Bromonitrobisethylenediamines*,  $[\text{Co en}_2(\text{NO}_2)\text{Br}]\text{X}$ , represented by the (1) Iodide; (2) Nitrite; and (3) Nitrate.
- (xlvii) *Bromonitrotetrammines*,  $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)\text{Br}]\text{X}$ , represented the bromide.
- (xlviii) *Bromonitrobisethylenediamines*,  $[\text{Co en}_2(\text{NO}_2)\text{Br}]\text{X}$ , represented by (1) Chloride; (2) Perchlorate; (3) Bromide; (4) Iodide; (5) Sulphate; (6) Persulphate; (7) Dithionate; (8) Nitrite; (9) Nitrate; (10) Thiocyanate; and (11) Camphorsulphonate.
- (xlix) *Bromochlorobisethylenediamines*,  $[\text{Co en}_2\text{ClBr}]\text{X}$ , represented by cis- and trans-salts, and some optically-active forms: (1) Chloride; (2) Bromide; (3) Sulphate; (4) Dithionate; (5) Nitrate; (6) Thiocyanate; and (7) Bromocamphorsulphonate.
- (l) *Bromochloroaquotriammines*,  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})\text{ClBr}]\text{X}$ , represented by the bromide.
- (li) *Bromochloroaquoethylenediamineammines*,  $[\text{Co}(\text{NH}_3)\text{en}(\text{H}_2\text{O})\text{ClBr}]\text{X}$ , represented by the bromide.
- (lii) *Hydrocarbonatonitrotetrammines*,  $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)(\text{HCO}_3)]\text{X}$ , represented by the nitrate.
- (liii) *Isothiocyanatohydroxybisethylenediamines*,  $[\text{Co en}_2(\text{OH})(\text{SCy})]\text{X}$ , represented by cis- and trans-thiocyanate.
- (liv) *Isothiocyanatonitrotetrammines*,  $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)(\text{SCy})]\text{X}$ , include (1) Hydroxide; (2) Chloride, and its double salt with silver and mer-

- cury; (3) Bromide; (4) Iodide; (5) Polyiodide; (6) Nitrite; (7) Nitrate; and (8) Oxalatodinitrodiammine.
- (lv) *Isothiocyanatonitrobisethylenediamines*,  $[\text{Co en}_2(\text{NO}_2)(\text{SCy})]\text{X}$ , represented by cis- and trans-salts, and some optically-active forms: (1) Chloride; (2) Perchlorate; (3) Bromide; (4) Iodide; (5) Sulphate; (6) Dithionate; (7) Nitrite; (8) Nitrate; and (9) Thiocyanate.
- (lvi) *Isothiocyanatonitritobisethylenediamines*,  $[\text{Co en}_2(\text{ONO})(\text{SCy})]\text{X}$ , represented by (1) Nitrate; and (2) Thiocyanate.
- (lvii) *Isothiocyanatochlorobisethylenediamines*,  $[\text{Co en}_2\text{Cl}(\text{SCy})]\text{X}$ , include cis- and trans-salts, and some optically-active forms: (1) Chloride; (2) Perchlorate; (3) Bromide; (4) Iodide; (5) Sulphate; (6) Dithionate; (7) Nitrite; (8) Nitrate; (9) Dichromate; (10) Thiocyanate; and (11) Bromocamphorsulphonate.
- (lviii) *Isothiocyanatobromobisethylenediamines*,  $[\text{Co en}_2\text{Br}(\text{SCy})]\text{X}$ , represented by cis- and trans-salts: (1) Perchlorate; (2) Bromide; (3) Sulphate; (4) Dithionate; (5) Nitrate; and (6) Thiocyanate.
- (lix) *Bisdimethylglyoximedianamines*,  $[\text{Co}(\text{NH}_3)_2\{\text{CH}_3\text{C}(\text{NOH})\text{C}(\text{NO})\text{CH}_3\}_2]\text{X}$ , represented by (1) Hydroxide; (2) Chloride; (3) Bromide; (4) Iodide; (5) Sulphate; (6) Selenate; (7) Nitrite; (8) Nitrate; and (9) Picrate.
- (lx) *Bisdimethylglyoximinebishydroxylamines*,  $[\text{Co}(\text{NH}_2\text{OH})_2\{\text{CH}_3\text{C}(\text{NO})\text{C}(\text{NOH})\text{CH}_3\}_2]\text{X}$ , include (1) Chloride; and (2) Iodide.
- (lxi) *Bisdimethylglyoximinbisethylamines*,  $[\text{Co}(\text{C}_2\text{H}_5\text{.NH}_2)_2\{\text{CH}_3\text{C}(\text{NO})\text{C}(\text{NOH})\text{CH}_3\}_2]\text{X}$ , include (1) Hydroxide; (2) Chloride; (3) Iodide; and (4) Nitrate.
- (lxii) *Bisdimethylglyoximebisanimines*,  $[\text{Co}(\text{C}_6\text{H}_5\text{.NH}_2)_2\{\text{CH}_3\text{C}(\text{NO})\text{C}(\text{NOH})\text{CH}_3\}_2]\text{X}$ , salts are known.
- (lxiii) *Bisdimethylglyoximinebis-p-toluidines*,  $[\text{Co}(\text{C}_7\text{H}_7\text{.NH}_2)_2\{\text{CH}_3\text{C}(\text{NO})\text{C}(\text{NOH})\text{CH}_3\}_2]\text{X}$ , salts are known.
- (lxiv) *Bisdimethylglyoximinebispyridines*,  $[\text{Co py}_2\{\text{CH}_3\text{C}(\text{NO})\text{C}(\text{NOH})\text{CH}_3\}_2]\text{X}$ , include (1) Hydroxide; (2) Chloride; (3) Iodide; (4) Nitrate; and (5) Thiocyanate.
- (lxv) *Bismonomethylglyoximinediammines*,  $[\text{Co}(\text{NH}_3)_2\{\text{CH}_3\text{C}(\text{NO})\text{C}(\text{NOH})\text{H}\}_2]\text{X}$ , represented by (1) Hydroxide; (2) Chloride; and (3) Iodide.
- (lxvi) *Sulphitobisethylenediamines*,  $[\text{Co en}_2(\text{SO}_3)]\text{X}$ , include (1) Chloride, and the double salts with gold, and platinum; (2) Bromide; and (3) Thiocyanate.
- (lxvii) *Sulphitoaquotriammines*,  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})(\text{SO}_3)]\text{X}$ , represented by the sulphite.
- (lxviii) *Sulphatobisethylenediamines*,  $[\text{Co en}_2(\text{SO}_4)]\text{X}$ , represented by the bromide.
- (lxix) *Thiosulphatobisethylenediamines*,  $[\text{Co en}_2(\text{S}_2\text{O}_3)]\text{X}$ , represented by the bromide.
- (lxx) *Carbonatotetrammines*,  $[\text{Co}(\text{NH}_3)_4(\text{CO}_3)]\text{X}$ , include (1) Hydroxide; (2) Fluoride; (3) Chloride, and the double salts with the chlorides of gold, and platinum; (4) Perchlorate; (5) Bromide, and a double salt with iridium bromide; (6) Iodide, and the double salts with mercury, and bismuth iodides; (7) Polyiodide; (8) Hydrosulphate; (9) Sulphate; (10) Dithionate; (11) Selenate; (12) Nitrate; (13) Carbonate; (14) Hydrocarbonate; (15) Chromate; (16) Dichromate; (17) Molybdate; (18) Tungstate; (19) Oxalate; (20) Trioxalato-cobaltate; (21) Malonate; and (22) Picrate.
- (lxxi) *Carbonatobisethylenediamines*,  $[\text{Co en}_2(\text{CO}_3)]\text{X}$ , include optically-active forms: (1) Hydroxide; (2) Chloride; (3) Bromide; (4) Iodide, and the double salts with silver, and mercury iodides; (5) Sulphate; (6) Dithionate; (7) Nitrate; and (8) Thiocyanate.

- (lxxii) *Carbonatobispropylenediamines*,  $[\text{Co pn}_2(\text{CO}_3)]\text{X}$ , represented by (1) Chloride; and (2) Nitrate.
- (lxxiii) *Carbonatobis(trimethylenediamines)*,  $[\text{Co}\{\text{NH}_2(\text{CH}_2)_3\text{NH}_2\}_2(\text{CO}_3)]\text{X}$ , represented by the chloride.
- (lxxiv) *Carbonatobisdiaminopentanes*,  $[\text{Co ptn}_2\text{CO}_3]\text{X}$ , represented by the chloride of the  $\alpha\beta\delta$ - and  $\beta\beta\delta$ -diaminopentanes.
- (lxxv) *Oxalatotetrammines*,  $[\text{Co}(\text{NH}_3)_4(\text{C}_2\text{O}_4)]\text{X}$ , include (1) Hydroxide; (2) Chloride, and double salts with the platinum chlorides; (3) Chlorate; (4) Perchlorate; (5) Bromide; (6) Sulphate; (7) Perchlorate; (8) Dithionate; (9) Selenate; (10) Nitrate; (11) Chromate; (12) Dichromate; (13) Oxalate; (14) Hydroxalate; (15) Trioxalatocobaltate; (16) Dioxalatodiamminocobaltate; (17) Oxalatodinitrodiamminocobaltate; and (18) Thiocyanatochromate.
- (lxxvi) *Oxalatobisethylenediamines*,  $[\text{Co en}_2(\text{C}_2\text{O}_4)]\text{X}$ , represented by some optically-active forms: (1) Hydroxide; (2) Chloride, and a double salt with gold chloride; (3) Perchlorate; (4) Bromide; (5) Iodide; (6) Sulphate; (7) Hydrosulphate; (8) Dithionate; (9) Selenate; (10) Nitrate; (11) Thiocyanate; (12) Dioxalatobisethylenediaminechromate; (13) Molybdate; and (14) Tungstate.
- (lxxvii) *Oxalatoaquotriammines*,  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})(\text{C}_2\text{O}_4)]\text{X}$ , include (1) Chloride; (2) Bromide; (3) Sulphate; (4) Dithionate; and (5) Nitrate.
- (lxxviii) *Oxalatobisdiaminopentanes*,  $[\text{Co ptn}_2(\text{C}_2\text{O}_4)]\text{X}$ , represented by the (1) Chloride; and the (2) Oxalate of the  $\alpha\beta\delta$ - and  $\beta\beta\delta$ -diaminopentanes.
- (lxxix) *Malonatotetrammines*,  $[\text{Co}(\text{NH}_3)_4(\text{C}_3\text{H}_2\text{O}_4)]\text{X}$ , represented by (1) Chloride, and a double salt with gold chloride; (2) Bromide; (3) Sulphate; (4) Dithionate; (5) Selenate; (6) Nitrate; (7) Thiocyanate; and (8) Hydromalonate.
- (lxxx) *Dimethylmalonatobisethylenediamines*,  $[\text{Co en}_2(\text{C}_5\text{H}_6\text{O}_4)]\text{X}$ , include (1) Chloride; (2) Bromide; and (3) Nitrate.
- (lxxx i) *Succinatobisethylenediamines*,  $[\text{Co en}_2(\text{C}_4\text{H}_4\text{O}_4)]\text{X}$ , include (1) Bromide; (2) Nitrate; and (3) Hydrosuccinate.
- (lxxx ii) *Dibromosuccinatobisethylenediamines*,  $[\text{Co en}_2(\text{C}_4\text{H}_2\text{O}_4\text{BrX}_2)]\text{X}$ , include (1) Bromide; (2) Nitrate; and (3) Dibromosuccinate.
- (lxxx iii) *Mesotartratobisethylenediamines*,  $[\text{Co en}_2(\text{C}_4\text{H}_4\text{O}_6)]\text{X}$ , include (1) Bromide; and (2) Hydromesotartrate.
- (lxxx iv) *Maleinatobisethylenediamines*,  $[\text{Co en}_2(\text{C}_4\text{H}_2\text{O}_4)]\text{X}$ , include (1) Bromide; (2) Nitrate; and (3) Hydromaleinate.
- (lxxx v) *Citraconatobisethylenediamines*,  $[\text{Co en}_2(\text{C}_5\text{H}_4\text{O}_4)]\text{X}$ , represented by the hydrocitraconate.
- (lxxx vi) *Itaconatobisethylenediamines*,  $[\text{Co en}_2(\text{C}_5\text{H}_4\text{O}_4)]\text{X}$ , represented by the hydroitaconate.
- (lxxx vii) *Phthalatobisethylenediamines*,  $[\text{Co en}_2(\text{C}_8\text{H}_4\text{O}_4)]\text{X}$ , include (1) Bromide; (2) Nitrate; and (3) Hydrophthalate.
- (lxxx viii) *Homophthalatobisethylenediamines*,  $[\text{Co en}_2(\text{C}_9\text{H}_6\text{O}_4)]\text{X}$ , include (1) Bromide; (2) Thiocyanate; and (3) Hydrohomophthalate.
- (lxxx ix) *Salicylatotetrammines*,  $[\text{Co}(\text{NH}_3)_4(\text{C}_7\text{H}_4\text{O}_3)]\text{X}$ , include (1) Chloride, and the double salt with platinum chloride; (2) Hydrochloride; (3) Hydroperchlorate; (4) Bromide; (5) Hydrobromide; (6) Iodide; (7) Hydroiodide; (8) Iodate; (9) Hydrosulphite; (10) Sulphate; (11) Hydrosulphate; (12) Thiosulphate; (13) Dithionate; (14) Hydrodithionate; (15) Tetrathionate; (16) Hydrotetrathionate; (17) Hydroselenite; (18) Nitrite; (19) Nitrate; (20) Hydronitrate; (21) Tetranitrodiamminocobaltate; (22) Carbonate; (23) Hydrocarbonate; (24) Fluosilicate; (25) Hydrofluosilicate; (26) Phosphite; (27) Hydrophosphate; (28) Pyrophosphate; (29) Hydropyrophosphate; (30) Hydropyroantimonate; (31) Hexacyanocobaltate;

- (32) Oxalate; (33) Hydroxalate; (34) Mesoxalate; (35) Dioxytartrate; (36) Picrate; and (37)  $\alpha$ -Naphthylamine- $\gamma$ -sulphonate.
- (xc) *Salicyatobisethylenediamines*,  $[\text{Co en}_2(\text{C}_7\text{H}_4\text{O}_3)]\text{X}$ , include (1) Chloride, and a double salt with mercury chloride; (2) Hydrochloride; (3) Bromide, and mercury bromide double salt; (4) Iodide, and mercury iodide double salt; (5) Nitrate; (6) Hydronitrate; (7) Carbonate; (8) Hydrocarbonate; and (9) Camphorsulphonate.
- (xci) *Sulphoacetatobisethylenediamines*,  $[\text{Co en}_2(\text{C}_2\text{H}_2\text{O}_5\text{S})]\text{X}$ , include (1) Chloride, and platinum chloride double salt; (2) Bromide; (3) Nitrate; (4) Thiocyanate; and (5) Hydrosulphoacetate.
- (xcii) *Benzylsulphoacetatobisethylenediamines*,  $[\text{Co en}_2(\text{C}_9\text{H}_8\text{O}_5\text{S})]\text{X}$ , include (1) Bromide; and (2) Benzylsulphoacetate.
- (xciii) *o-Sulphobenzoatobisethylenediamines*,  $[\text{Co en}_2(\text{C}_7\text{H}_4\text{O}_5\text{S})]\text{X}$ , include (1) Bromide; and (2) Hydrosulphobenzoate.
- (xciv) *Sulphonyldiacetatobisethylenediamines*,  $[\text{Co en}_2(\text{C}_4\text{H}_4\text{O}_6\text{S})]\text{X}$ , include (1) Chloride, and double salts with gold, and platinum chlorides; (2) Bromide; (3) Iodide; (4) Dithionate; (5) Nitrate; (6) Thiocyanate; (7) Hydrosulphonyldiacetate.
- (xcv) *Methionatobisethylenediamines*,  $[\text{Co en}_2(\text{CH}_2\text{O}_6\text{S}_2)]\text{X}$ , include (1) Chloride, and platinum chloride double salt; (2) Bromide; (3) Nitrate; (4) Thiocyanate; and (5) Methionate.
- (xcvi) *Bromobenzene-3:4-disulphonatobisethylenediamines*,  $[\text{Co en}_2(\text{C}_6\text{H}_3\text{O}_6\text{BrS}_2)]\text{X}$ , represented by the Bromobenzene-3:4-disulphonate.
- (xcvii) *Ethylenediaminediacetylacetonatodiammines*,  $[\text{Co}(\text{NH}_3)_2(\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}_2)]\text{X}$ , include (1) Chloride; (2) Chlorate; (3) Perchlorate; (4) Bromide; (5) Iodide; (6) Nitrite; (7) Nitrate; and (8) Camphorsulphonate.
- (xcviii) *Chromatotetrammines*,  $[\text{Co}(\text{NH}_3)_4(\text{CrO}_4)]\text{X}$ , include (1) Nitrate; (2) Chromate; and (3) Dichromate.
- (xcix) *Chromatotaquotriammines*,  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})(\text{CrO}_4)]\text{X}$ , are represented by the dichromate.
- (c) *Molybdatotetrammines*,  $[\text{Co}(\text{NH}_3)_4(\text{MoO}_4)]\text{X}$ , include (1) Nitrate; (2) Molybdate; and (3) Trimolybdate.
- (ci) *Dimolybdatotetrammines*,  $[\text{Co}(\text{NH}_3)_4(\text{Mo}_2\text{O}_7)]\text{X}$ , are represented by the trimolybdate.
- (cii) *Phosphatotetrammine*,  $[\text{Co}(\text{NH}_3)_4(\text{PO}_4)]$ .
- (ciii) *Trischromatobistetrammines*,  $[\{\text{Co}(\text{NH}_3)_4\}_2(\text{CrO}_4)_3]$ .
- (civ) *Sulphitohydroxytetrammine*,  $[\text{Co}(\text{NH}_3)_4(\text{OH})(\text{SO}_3)]$ .
- (cv) *Sulphitonitrotetrammine*,  $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)(\text{SO}_3)]$ .
- (cvi) *Oxalatochloroquatriammine*,  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})\text{Cl}(\text{C}_2\text{O}_4)]$ .
- (cvii) *Disulphitotetrammines*,  $\text{M}[\text{Co}(\text{NH}_3)_4(\text{SO}_3)_2]$ , include cis- and trans-salts: (1) Lithium; (2) Sodium; (3) Ammonium, and double salts with ammonium and barium sulphites; (4) Potassium; (5) Rubidium; (6) Cæsium; (7) Barium; (8) Cobaltous; and (9) Cobaltic salts.
- (cviii) *Disulphitobisethylenediamines*,  $\text{M}[\text{Co en}_2(\text{SO}_3)_2]$ , include (1) Sodium; (2) Ammonium; and (3) Strychnine salts.
- (cix) *Disulphitoethylenediaminediammines*,  $\text{M}[\text{Co}(\text{NH}_3)_2\text{en}(\text{SO}_3)_2]$ , represented by the ammonium salt.
- (cx) *Disulphitobispropylenediamines*,  $\text{M}[\text{Co pn}_2(\text{SO}_3)_2]$ , represented by the ammonium salt.
- (cxi) *Disulphitoaquotriammines*,  $\text{M}[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})(\text{SO}_3)_2]$ , represented by (1) Hydrogen salt, i.e. the acid, and (2) Sodium salt.
- (cxii) *Bischromatotetrammines*,  $\text{M}[\text{Co}(\text{NH}_3)_4(\text{CrO}_4)_2]$ , include (1) Lithium; (2) Sodium; (3) Potassium; and (4) Magnesium salts.
- (cxiii) *Bisdimethylglyoximatediamine*, including the (1) Chloride; (2) Bromide; (3) Iodide; (4) Sulphate; and (5) Thiocyanate.

IV.—**The triammine family**, or compounds of the null-valent group, which, with a simple univalent acidic radicle,  $X'$ , can be symbolized,  $[CoA_3X_3']$ . There are further complications with the introduction of a bivalent radicle,  $Y''$ , and only a few types have been investigated.

- (i) *Compounds of the type*  $[CoA_3X_3']$ , include (1) Trinitrotriammine; (2) Trinitroethylenediamineammine; (3) Trinitropropylenediamineammine; (4) Trinitratotriammine; (5) Trichlorotriammine; (6) Tribromotriammine; (7) Chlorodinitrotriammine; (8) Bromodinitrotriammine; and (9) Dihydroxytetranitrotrihydrazine. There is also a series of complexes built up with (1) Dimethylglyoxime,  $CH_3C(NO)(OH)CH_3$ ; and also series with (2) Monomethylglyoxime,  $HC(NO)(OH)CH_3$ ; with (3) Methylglyoxime,  $CH_3C(NO)(OH)C_2H_5$ ; with (4)  $\alpha$ - and  $\beta$ -benzylmonoximes,  $C_6H_5.C(NO)(OH).CO.C_6H_5$ ; with (5) Glycine,  $NH_2CH_2CO$ ; with (6) alanine,  $CH_3.CH(NH_2).COOH$ ; with (7) Methylalanine,  $CH_3.CH(NH_2).COOCH_3$ ; with (8) Picolonic acid,  $C_5H_4N(COOH)$ ; with (9) Dithiocarbamate,  $NH_2.CS_2H$ ; with (10) Dimethyldithiocarbamate,  $N(CH_3)_2.CS_2H$ ; with (11) Di-*iso*-butyldithiocarbamate,  $N(C_4H_9)_2.CS_2H$ ; (12) Phenyldithiocarbamate,  $NH(C_6H_5).CS_2H$ ; (13) with 2:2'-pyridylpyrrole,  $(CH_3CH_2)_2N.C_5H_4N$ ; (14) with pyrrole-2-methylimide,  $C_4H_4.N.CH:NCH_3$ ; (15) with 2-pyridylmethylketoxime,  $(C_4H_4N.CH)(NO)C_4H_3$ ; and with (16) Diazoaminotoluene,  $C_7H_7.N_2.NH.C_7H_7$ .
- (ii) *Compounds of the type*,  $[(CoA_3)_2Y_3']$ , include (1) Sulphodithiocarbonatohexammine,  $[Co(NH_3)_3)_2(CS_3)_2S]$ ; (2) Thiosulphatodithiocarbonatohexammine,  $[Co(NH_3)_3)_2(CS_3)_2(S_2O_3)]$ ; (3) Tricarbonatohexammine,  $[Co(NH_3)_3)_2(CO_3)_3]$ ; (4) Trioxalatobisethylenediaminediammine,  $[Co(NH_3)_3)_2(C_2O_4)_3]$ ; and (5) Trirubeanatotetraquodiammine,  $[Co(NH_3)(H_2O)_2)_2(C_2N_2S_2H_2)_3]$ .
- (iii) *Compounds of the type*,  $[CoA_3Y''X']$ , include (1) Hydroxychromatotriammine,  $[Co(NH_3)_3(CrO_4)(OH)]$ ; (2) Hydrosulphothiocarbonatotriammine,  $[Co(NH_3)_3(CS_3)(HS)]$ ; (3) Isothiocyanatolatotriammine,  $[Co(NH_3)_3(C_2O_4)(SCy)]$ ; (4) Hydroxyoxalatotriammine,  $[Co(NH_3)_3(C_2O_4)(OH)]$ ; (5) Nitroxalatotriammine,  $[Co(NH_3)_3(C_2O_4)(NO_2)]$ ; and (6) Chloroxalatotriammine,  $[Co(NH_3)_3(C_2O_4)Cl]$ .
- (iv) *Compounds of the type*  $[(CoA_3)_2Y''X_4']$ , include (1) Tetranitrosulphatohexammine,  $[Co(NH_3)_3)_2(SO_4)(NO_2)_4]$ ; and (2) Tetranitroselenatohexammine,  $[Co(NH_3)_3)_2(SeO_4)(NO_2)_4]$ .
- (v) *Compounds of the type*,  $M[CoA_3Y_2']$ , include Dioxalatotriaminocobaltic acid,  $H[Co(NH_3)_3(C_2O_4)_2].2H_2O$ , and the sodium, ammonium, potassium, pyridine, trans-dinitrotetrammine, and dichloroaquotriammine salts.
- (vi) *Compounds of the type*,  $M_3[CoA_3Y_3']$ , include (1) the Trisulphitotriaminocobaltates of ammonium and cobalt(ie); (2) Trisulphitoaquodiamminocobaltates represented by the cobaltic salt; and the dextro- and lævo-forms of asparaginic acid.

G. T. Morgan and co-workers discussed the metallic lakes of the orthoquinona oximes which form a group of mordant dyes, many of which furnish cobaltic derivatives—*e.g.*, nitroso- $\beta$ -naphthol, alizarin, dinitrosoresorcinol, and the azosalicylic acids. The cobalt atom is implicated in a heterocyclic ring both by the principal and supplementary valencies.

V.—**The diammine family**, or compounds of the univalent acidic group:  $[CoA_2X_4']$ .

- (i) *Tetranitrodiamminocobaltates*,  $M[Co(NH_3)_2(NO_2)_4]$ , which include the salts: (1) Sodium; (2) Ammonium; (3) Tetramethylammonium; (4) Potassium; (5) Rubidium; (6) Cæsium; (7) Copper; (8) Silver;

- (9) Zinc ; (10) Mercury ; (11) Thallium ; (12) Lead ; (13) Dichlorotetraquochromate ; (14) Dibromotetraquochromate ; (15) Hexacarbamidochromate ; (16) Hexamminocobaltate ; (17) Hydroxypentamminocobaltate ; (18) Chloropentamminocobaltate ; (19) Bromoaquobisethylenediaminocobaltate ; (20) Nitropentamminocobaltic ; (21) Nitroaquopentamminocobaltate ; (22) Nitratopentamminocobaltate ; (23) Dichloroquaterpyridinecobaltate ; (24) Dichloro-aquotriamminocobaltate ; (25) Dinitrotetramminocobaltic—*cis*- and *trans*- ; (26) Carbonatotetramminocobaltate ; (27) Oxalatotetramminocobaltate ; (28) Salicylatotetramminocobaltate ; and (29) Nickel.
- (ii) *Tetranitrobis-p-toluidinecobaltates*,  $M[Co(C_7H_7.NH_2)_2(NO_2)_4]$ , represented by the *p*-toluidine salt.
- (iii) *Dichlorodinitrodiamminocobaltates*,  $M[Co(NH_3)_2(NO_2)_2Cl_2]$ , represented by the salt with chloronitrotetrammine.
- (iv) *Dinitrobisdimethylglyoximinocobaltates*,  $M[Co\{CH_3C(NO)C(NO)CH_3\}_2(NO_2)_2]$ , represented by the acid  $H[Co\{CH_3C(NO)C(NO)CH_3\}_2(NO_2)_2].H_2O$ , and the (1) Sodium ; (2) Ammonium ; (3) Ethylammonium ; and (4) Bisisobutylammonium salts.
- (v) *Disulphitodiamminocobaltates*,  $M[Co(NH_3)_2(SO_3)_2]$ , represented by (1) Sodium ; (2) Ammonium ; and (3) Strychnine salts.
- (vi) *Dioxalatodiamminocobaltates*,  $M[Co(NH_3)_2(C_2O_4)_2]$ , represented by the acid,  $H[Co(NH_3)_2(C_2O_4)_2]$ , and (1) Ammonium ; (2) Potassium ; (3) Barium ; (4) Cobaltous ; (5) Acid cobaltous ; (6) *trans*-Dinitrotetramminecobaltate ; (7) *trans*-Dichlorotetramminocobaltate ; (8) Oxalatotetramminocobaltate ; and (9) Strychnine salts.
- (vii) *Dioxalatoethylenediaminecobaltate*,  $M[Co en(C_2O_4)_2]$ , represented by the oxalatobisethylenediaminechromate.
- (viii) *Dinitrooxalatodiamminocobaltates*,  $M[Co(NH_3)_2(C_2O_4)(NO_2)_2]$ , represented by the acid,  $H[Co(NH_3)_2(C_2O_4)(NO_2)_2]$ , and the *cis*- and *trans*-salts of (1) Sodium ; (2) Ammonium ; (3) Ethylenediammonium ; (4) Phenylethylammonium ; (5) Copper ; (6) Silver ; (7) Barium ; (8) Magnesium ; (9) Ammonium magnesium ; (10) Zinc ; (11) Cadmium ; (12) Thallium ; (13) Cobaltous ; (14) Ammonium cobaltous ; (15) Potassium cobaltous ; (16) Silver cobaltous ; (17) Hexamminocobaltic ; (18) Aquopentamminocobaltic ; (19) Diaquotetramminocobaltic ; (20) *cis*-Dinitrotetramminocobaltic ; (21) Oxalatotetramminocobaltic ; (22) *iso*-Thiocyanatonitrotetramminocobaltic ; (23) Nickel ; and (24) Strychnine.
- (ix) *Dinitromalonatodiamminocobaltates*,  $M[Co(NH_3)_2(C_3H_2O_4)(NO_2)_2]$ , represented by the barium salt.
- (x) *Oxalatobisdinitrobisdiamminocobaltate*,  $[Co(NH_3)_2(NO_2)_2]_2(C_2O_4)$ .

VI.—**The monammine family**, or compounds of the bivalent, acidic group :  $[CoA_5X]''$ .

This is represented by sodium pentametanitratomonamminocobaltate,  $Na_2[Co(NH_3)(NO_2)_2]$ .

VII.—**The hexa-acid family**, or compounds of the tervalent acidic group :  $[CoX_6]'''$ , represented by hexanitritocobaltic acid,  $H_3[Co(NO_2)_6]$ , and its salts ; hexacyanocobaltic acid,  $H_3[CoCy_6]$  ; pentacyanothiosulphatocobaltic acid,  $H_4[CoCy_5(S_2O_3)]$  ; potassium trisoxalatocobaltate,  $K_3[Co(C_2O_4)_3]$  ; thio-sulphatopentacyanocobaltic acid,  $H_4[CoCy_5(S_2O_3)]$ , etc.

*B.—Compounds with more than one atom of Cobalt in the nucleus.*

I.—**Dicobaltic salts**—with two cobalt atoms in the nucleus. Cobaltic melanochloride, and cobaltic fusco-salts have been previously discussed.

- (i) *Peroxo-decammines* with two tervalent cobalt atoms,  $[(NH_3)_5Co$

- O<sub>2</sub>—Co(NH<sub>3</sub>)<sub>5</sub>]X<sub>4</sub>, include (1) Hydroxide; (2) Chloride; (3) Iodide; (4) Sulphate; (5) Hydrosulphate; (6) Chlorosulphate; (7) Selenate; (8) Hydroselenate; (9) Nitrate; (10) Hydronitrate; (11) Hydrochloronitrate; (12) Sulphatonitrate; (13) Cyanate; (14) Thiocyanate; and (15) Nitratothiocyanate.
- (ii) *Peroxo-decammines* with one tervalent and one quadrivalent cobalt atom, [(NH<sub>3</sub>)<sub>5</sub>Co—O<sub>2</sub>—Co(NH<sub>3</sub>)<sub>5</sub>]X<sub>5</sub>, include (1) Chloride, and its double salt with platinum chloride; (2) Sulphate; (3) Hydrosulphate; (4) Chlorosulphate; (5) Selenate; (6) Nitrate; (7) Chloronitrate; (8) Sulphatonitrate; and (9) Dichromate.
- (iii) *Trichlorohydroxy-peroxo-hexammines*, [Cl<sub>2</sub>(NH<sub>3</sub>)<sub>3</sub>Co—O<sub>2</sub>—Co(NH<sub>3</sub>)<sub>3</sub>—(OH)Cl]X, represented by the (1) Chloride, and (2) Nitrate.
- (iv) *Sulphato-μ-imino-octammines*, [(NH<sub>3</sub>)<sub>4</sub>Co=(NH)(SO<sub>4</sub>)=Co(NH<sub>3</sub>)<sub>4</sub>]X<sub>2</sub>, represented by the (1) Chloride, and (2) Nitrate.
- (v) *μ-Amino-decammines*, [(NH<sub>3</sub>)<sub>5</sub>Co—NH<sub>2</sub>⋯Co(NH<sub>3</sub>)<sub>5</sub>]X<sub>5</sub>, include (1) Chloride; (2) Bromide; (3) Sulphate; (4) Dithionate; (5) Selenate; and (6) Nitrate.
- (vi) *Nitratoaquo-μ-amino-octammines*, [(H<sub>2</sub>O)(NH<sub>3</sub>)<sub>4</sub>⋯NH<sub>2</sub>—Co(NH<sub>3</sub>)<sub>4</sub>—(NO<sub>3</sub>)]X<sub>4</sub>, represented by the nitrate.
- (vii) *Chloroaquo-μ-amino-octammines*, [(H<sub>2</sub>O)(NH<sub>3</sub>)<sub>4</sub>Co—NH<sub>2</sub>⋯Co(NH<sub>3</sub>)<sub>4</sub>—Cl]X<sub>4</sub>, include (1) Chloride; (2) Sulphate; (3) Dithionate; and (4) Selenate.
- (viii) *Chloronitrato-μ-amino-octammines*, [Cl(NH<sub>3</sub>)<sub>4</sub>Co—NH<sub>2</sub>⋯Co(NH<sub>3</sub>)<sub>4</sub>—(NO<sub>3</sub>)]X<sub>3</sub>, represented by the nitrate.
- (ix) *Bromoaquo-μ-amino-octammines*, [(H<sub>2</sub>O)(NH<sub>3</sub>)<sub>4</sub>Co—NH<sub>2</sub>⋯Co(NH<sub>3</sub>)<sub>4</sub>—Br]X<sub>4</sub>, represented by (1) Bromide; and (2) Sulphate.
- (x) *Thiocyanatochloro-μ-amino-octammines*, [(SCy)(NH<sub>3</sub>)<sub>4</sub>Co—NH<sub>2</sub>⋯Co(NH<sub>3</sub>)<sub>4</sub>Cl]X<sub>3</sub>, represented by the thiocyanate.
- (xi) *Sulphato-μ-amino-octammines*, [(NH<sub>3</sub>)<sub>4</sub>Co=(NH<sub>2</sub>)(SO<sub>4</sub>)⋯Co(NH<sub>3</sub>)<sub>4</sub>]X<sub>3</sub>, include (1) Chloride; (2) Bromide; (3) Iodide; (4) Hydrosulphate; (5) Hydroselenate; (6) Nitrate; and (7) Chloronitrate.
- (xii) *Sulphato-μ-amino-quaterethylenediamines*, [en<sub>2</sub>Co=(NH<sub>2</sub>)(SO<sub>4</sub>)⋯Co en<sub>2</sub>]X<sub>3</sub>, include some optically-active forms: (1) Bromide; (2) Nitrate; (3) Thiocyanate; and (4) Bromocamphorsulphonate.
- (xiii) *Selenato-μ-amino-octammines*, [(NH<sub>3</sub>)<sub>4</sub>Co=(NH<sub>2</sub>)(SeO<sub>4</sub>)⋯Co(NH<sub>3</sub>)<sub>4</sub>]X<sub>3</sub>, include (1) Hydrosulphate; (2) Hydroselenate; and (3) Nitrate.
- (xiv) *Tetrachloro-μ-amino-hexammine*, [Cl<sub>2</sub>(NH<sub>3</sub>)<sub>3</sub>Co—NH<sub>2</sub>⋯Co(NH<sub>3</sub>)<sub>3</sub>Cl<sub>2</sub>]X, represented by the chloride.
- (xv) *Tetrabromo-μ-amino-hexammines*, [Br<sub>2</sub>(NH<sub>3</sub>)<sub>3</sub>Co—NH<sub>2</sub>⋯Co(NH<sub>3</sub>)<sub>3</sub>—Br<sub>2</sub>]X, represented by (1) Bromide; and (2) Nitrate.
- (xvi) *Trichloroaquo-μ-amino-hexammines*, [Cl<sub>2</sub>(NH<sub>3</sub>)<sub>3</sub>Co—NH<sub>2</sub>⋯Co(NH<sub>3</sub>)<sub>3</sub>—(H<sub>2</sub>O)Cl]X<sub>2</sub>, represented by the chloride.
- (xvii) *Trichloronitrato-μ-amino-hexammines*, [Cl<sub>2</sub>(NH<sub>3</sub>)<sub>3</sub>Co—NH<sub>2</sub>⋯Co(NH<sub>3</sub>)<sub>3</sub>—(NO<sub>3</sub>)Cl]X, represented by the nitrate.
- (xviii) *Diol-octammines*, [(NH<sub>3</sub>)<sub>4</sub>Co⋯(OH)<sub>2</sub>⋯Co(NH<sub>3</sub>)<sub>4</sub>]X<sub>4</sub>, include (1) Chloride, and the double salts with gold, and platinum chlorides; (2) Chlorate; (3) Bromide; (4) Bromate; (5) Iodide; (6) Iodate; (7) Sulphate; (8) Dithionate; (9) Selenate; (10) Nitrate; (11) Fluosilicate; (12) Phosphate; (13) Chromate; (14) Oxalate; and (15) Thiocyanate.
- (xix) *Diol-quaterethylenediamines*, [en<sub>2</sub>Co⋯(OH)<sub>2</sub>⋯Co en<sub>2</sub>]X<sub>4</sub>, include (1) Chloride; (2) Bromide; (3) Iodide; (4) Dithionate; (5) Nitrate; (6) Chromate; (7) Dithionate; (8) Oxalate; and (9) Thiocyanate.
- (xx) *Dinitrato-diol-hexammines*, [(NO<sub>3</sub>)(NH<sub>3</sub>)<sub>3</sub>Co⋯(OH)<sub>2</sub>⋯Co(NH<sub>3</sub>)<sub>3</sub>(NO<sub>3</sub>)]X<sub>2</sub>, represented by the nitrate.
- (xxi) *Diaquo-diol-hexammines*, [(H<sub>2</sub>O)(NH<sub>3</sub>)<sub>3</sub>Co⋯(OH)<sub>2</sub>⋯Co(NH<sub>3</sub>)<sub>3</sub>(H<sub>2</sub>O)]X<sub>4</sub>, represented by the sulphate.

- (xxii) *Nitratoquo-diol-hexammines*,  $[(\text{H}_2\text{O})(\text{NH}_3)_3\text{Co}\cdots(\text{OH})_2\cdots\text{Co}(\text{NH}_3)_3\cdots(\text{NO}_3)]\text{X}_3$ , represented by the dithionate.
- (xxiii)  $\mu$ -*Diamino-octammines*,  $[(\text{NH}_3)_4\text{Co}\cdots(\text{NH}_2)_2\cdots\text{Co}(\text{NH}_3)_4]\text{X}_4$ , represented by (1) Bromide; and (2) Dithionate.
- (xxiv) *Hydroxyaquo-peroxo-ol-hexammines*,  $[(\text{OH})(\text{NH}_3)_3\text{Co}=(\text{OH})(\text{O}_2)\cdots\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})]\text{X}_3$ , include (1) Chloride; (2) Bromide; (3) Sulphate, and the double salt with ammonium sulphate; and (4) Nitrate.
- (xxv)  $\mu$ -*Imino-peroxo-quaterethylenediamines*,  $[\text{en}_2\text{Co}=(\text{O}_2)(\text{NH})=\text{Co en}_2]\text{X}_3$ , include some optically-active forms: (1) Chloride; (2) Iodide; and (3) Nitrate.
- (xxvi)  $\mu$ -*Ammonium-peroxo-quaterethylenediamines*,  $[\text{en}_2\text{Co}=(\text{O}_2)(\text{NH}_4.\text{HX})=\text{Co en}_2]\text{X}$ , include some optically-active forms: (1) Bromide; (2) Dithionate; and (3) Nitrate.
- (xxvii)  $\mu$ -*Amino-peroxo-octammines*,  $[(\text{NH}_3)_4\text{Co}=(\text{NH}_2)(\text{O}_2)\cdots\text{Co}(\text{NH}_3)_4]\text{X}_4$ , include (1) Chloride; (2) Bromide; (3) Sulphate; (4) Dithionate; (5) Selenate; (6) Nitrate.
- (xxviii)  $\mu$ -*Amino-peroxo-quaterethylenediamines*,  $[\text{en}_2\text{Co}=(\text{NH}_2)(\text{O}_2)\cdots\text{Co en}_2]\text{X}_4$ , include some optically-active forms: (1) Chloride, and a double salt with platinum chloride; (2) Bromide; (3) Dithionate; (4) Nitrate; and (5) Bromocamphorsulphonate.
- (xxix) *Dichloro- $\mu$ -amino-peroxo-hexammines*, in isomeric forms, symmetrical,  $[\text{Cl}(\text{NH}_3)_3\text{Co}=(\text{NH}_2)(\text{O}_2)\cdots\text{Co}(\text{NH}_3)_3\text{Cl}]\text{X}_2$ , and asymmetrical,  $[(\text{NH}_3)_4\text{Co}=(\text{NH}_2)(\text{O}_2)\cdots\text{Co}(\text{NH}_3)_2\text{Cl}_2]\text{X}_2$ , and represented by (1) Chloride; and (2) Nitrate.
- (xxx) *Dibromo- $\mu$ -amino-peroxo-hexammines*, in isomeric forms, symmetrical,  $[\text{Br}(\text{NH}_3)_3\text{Co}=(\text{NH}_2)(\text{O}_2)\cdots\text{Co}(\text{NH}_3)_3\text{Br}]\text{X}_2$ , and asymmetrical,  $[(\text{NH}_3)_4\text{Co}=(\text{NH}_2)(\text{O}_2)\cdots\text{Co}(\text{NH}_3)_2\text{Br}_2]\text{X}_2$ , and represented by the bromide.
- (xxxi)  $\mu$ -*Amino-ol-octammines*,  $[(\text{NH}_3)_4\text{Co}=(\text{NH}_2)(\text{OH})\cdots\text{Co}(\text{NH}_3)_4]\text{X}_4$ , include (1) Chloride; (2) Bromide; (3) Sulphate; (4) Dithionate; (5) Selenate; (6) Nitrate; and (7) Thiocyanate.
- (xxxii)  $\mu$ -*Amino-ol-quaterethylenediamines*,  $[\text{en}_2\text{Co}\cdots(\text{NH}_2)(\text{OH})=\text{Co en}_2]\text{X}_4$ , include some optically-active forms: (1) Bromide; and (2) Iodide.
- (xxxiii) *Diaquo- $\mu$ -amino-ol-hexammines*,  $[(\text{H}_2\text{O})(\text{NH}_3)_3\text{Co}\cdots(\text{NH}_2)(\text{OH})\cdots\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})]\text{X}_4$ , represented by the nitrate.
- (xxxiv) *Nitratoquo- $\mu$ -amino-ol-hexammines*,  $[(\text{H}_2\text{O})(\text{NH}_3)_3\text{Co}\cdots(\text{NH}_2)(\text{OH})\cdots\text{Co}(\text{NH}_3)_3(\text{NO}_3)]\text{X}_3$ , include (1) Chloride; (2) Bromide; and (3) Nitrate.
- (xxxv) *Dichloro- $\mu$ -nitro-ol-hexammines*,  $[\text{Cl}(\text{NH}_3)_3\text{Co}\cdots(\text{NO}_2)(\text{OH})\cdots\text{Co}(\text{NH}_3)_3\cdots\text{Cl}]\text{X}_2$ , include (1) Chloride; (2) Sulphate; (3) Dithionate; and (4) Nitrate.
- (xxxvi) *Dibromo- $\mu$ -nitro-ol-hexammines*,  $[\text{Br}(\text{NH}_3)_3\text{Co}\cdots(\text{NO}_2)(\text{OH})\cdots\text{Co}(\text{NH}_3)_3\cdots\text{Br}]\text{X}_2$ , include (1) Bromide; (2) Dithionate; and (3) Nitrate.
- (xxxvii)  $\mu$ -*Amino-nitro-octammines*,  $[(\text{NH}_3)_4\text{Co}\cdots(\text{NH}_2)(\text{NO}_2)\cdots\text{Co}(\text{NH}_3)_4]\text{X}_4$ , include (1) Chloride; (2) Bromide; (3) Iodide; (4) Sulphate; (5) Selenate; and (6) Nitrate.
- (xxxviii)  $\mu$ -*Amino-nitro-quaterethylenediamines*,  $[\text{en}_2\text{Co}\cdots(\text{NH}_2)(\text{NO}_2)\cdots\text{Co en}_2]\text{X}_4$ , include some optically-active forms: (1) Bromide; (2) Iodide; (3) Nitrate; (4) Thiocyanate; and (5) Bromocamphorsulphonate.
- (xxxix) *Dichloro- $\mu$ -amino-nitrohexammines*,  $[\text{Cl}(\text{NH}_3)_3\text{Co}\cdots(\text{NO}_2)(\text{NH}_2)\cdots\text{Co}(\text{NH}_3)_3\text{Cl}]\text{X}_2$ , include (1) Chloride; and (2) Nitrate.
- (xl) *Acetatoaquo- $\mu$ -acetato-ol-hexammines*,  $[(\text{H}_2\text{O})(\text{NH}_3)_3\text{Co}\cdots\{\text{OC}(\text{CH}_3)\text{O}\}\text{OH}\cdots\text{Co}(\text{NH}_3)_3(\text{C}_2\text{H}_3\text{O}_2)]\text{X}_3$ , represented by the bromide.
- (xli) *Diaquo- $\mu$ -acetato-amino-hexammines*,  $[(\text{H}_2\text{O})(\text{NH}_3)_3\text{Co}\cdots(\text{NH}_2)\{\text{OC}(\text{CH}_3)\text{O}\}\cdots\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})]\text{X}_4$ , include (1) Bromide; and (2) Nitrate.
- (xlii) *Triol-hexammines*,  $[(\text{NH}_3)_3\text{Co}\cdots(\text{OH})_3\cdots\text{Co}(\text{NH}_3)_3]\text{X}_3$ , include (1)



- Chloride; (2) Bromide; (3) Sulphate; (4) Thiosulphate; (5) Dithionate; (6) Selenate; (7) Nitrate; and (8) Thiocyanate.
- (xliii) *Peroxo-diol-seriespropylamine*,  $[(C_7H_7.NH_2)_3 \cdots (OH)_2(O_2) \cdots Co(C_7H_7.NH_2)_3]X_3$ , represented by the chloride.
- (xliv) *Peroxo-diol-seriesallylamines*,  $[(C_3H_5.NH_2)_3 \cdots (OH)_2(O_2) \cdots Co(C_3H_5.NH_2)_3]X_3$ , include (1) Chloride; and (2) Nitrate.
- (xlv) *Peroxo-diol-seriesbenzylamine*,  $[C_6H_5.CH_2.NH_2)_3 \cdots (OH)_2(O_2) \cdots Co(C_6H_5.CH_2.NH_2)_3]X_3$ , represented by the chloride.
- (xlv)  $\mu$ -*Amino-diol-hexammines*,  $[(NH_3)_3Co \cdots (NH_2)(OH)_2 \cdots Co(NH_3)_3]X_3$ , include (1) Chloride; (2) Bromide; (3) Iodide; and (4) Nitrate.
- (xlvii)  $\mu$ -*Nitro-diol-hexammines*,  $[(NH_3)_3Co \cdots (NO_2)(OH)_2 \cdots Co(NH_3)_3]X_3$ , include (1) Chloride; (2) Bromide; (3) Sulphate; (4) Selenate; and (5) Nitrate.
- (xlviii)  $\mu$ -*Dinitro-ol-hexammines*,  $[(NH_3)_3Co \cdots (NO_2)_2(OH) \cdots Co(NH_3)_3]X_3$ , include (1) Chloride; and (2) Nitrate.
- (xlix)  $\mu$ -*Acetato-diol-hexammines*,  $[(NH_3)_3Co \cdots (OH)_2\{OC(CH_3)O\} \cdots Co(NH_3)_3]X_3$ , include (1) Chloride; (2) Bromide; (3) Iodide; (4) Nitrate; (5) Bromodithionate; and (6) Thiocyanate.
- (l)  $\mu$ -*Amino-ol-peroxo-hexammines*,  $[(NH_3)_3Co \cdots (NH_2)(OH)(O_2) \cdots Co(NH_3)_3]X_3$ , include (1) Chloride; (2) Bromide; and (3) Nitrate.
- (li)  $\mu$ -*Acetato-amino-ol-hexammines*,  $[(NH_3)_3Co \cdots (NH_2)(OH)\{OC(CH_3)O\} \cdots Co(NH_3)_3]X_3$ , include (1) Chloride, and its double salt with platinum; (2) Bromide; (3) Iodide; (4) Nitrate; and (5) Thiocyanate.

## II.—Tricobaltic salts, with three cobalt atoms in the nucleus.

- (i) *Diaquo-tetrol-quaterethylenediamines*,  $[en_2Co=(OH)_2Co(H_2O)_2 \cdots (OH)_2=Co en_2]X_4$ , represented by (1) Chloride, and its double salt with platinum chloride; (2) Iodide; (3) Sulphate; and (4) Dithionate.
- (ii) *Diaquo-pentol-hexammines*,  $[(H_2O)(NH_3)_3Co=(OH)_2(H_2O) \cdots Co \cdots (OH)_3 \equiv Co(NH_3)_3]X_4$ , represented by the chloride.
- (iii) *Hexol-hexammines*,  $[(NH_3)_3Co \geq (OH)_3 \cdots Co \cdots (OH)_3 \equiv Co(NH_3)_3]X_3$ , include (1) Chloride; (2) Bromide; (3) Sulphate; and (4) Dithionate.
- (iv) *Diphosphatobisethylenediamines*, represented by the phosphate.
- (v) *Diphosphatobispropylenediamines*, represented by the phosphate.

## III.—Tetracobaltic salts, with four cobalt atoms in the nucleus.

- (i) *Hexol-dodecammines*,  $[Co\{(OH)_2=Co(NH_3)_4\}_3]X_6$ , include some optically-active forms: (1) Chloride, and a double salt with platinum chloride; (2) Bromide; (3) Sulphate; (4) Thiosulphate; (5) Dithionate; (6) Selenate; (7) Nitrate; (8) Fluosilicate; (9) Molybdate; (10) Bromocamphorsulphonate; (11) Picrate; and (12) Dipicrylamide.
- (ii) *Hexol-seriesethylenediamines*,  $[Co\{(OH)_2=Co en_2\}_3]X_6$ , include (1) Chloride; (2) Bromide; (3) Iodide; (4) Nitrate; and (5) Thiocyanate.

There is a number of salts whose constitution is unknown; there are several possible explanations. In some cases the results have not been checked up under the guidance of the theory. The theory would have made the investigators extra critical in the case of indecisive results. There are the oxy-salts of G. Künzel,<sup>3</sup> namely,  $Co_4(NH_3)_{20}O(NO_3)_{10}$ , and  $Co_2(NH_3)_8O(S_2O_6)_2$ ; E. Frémy's  $Co_3(NH_3)_2O_2Cl_2.5H_2O$ ; S. P. L. Sørensen's  $Co_2O(NH_3)_4(C_2O_4)_2.2H_2O$ , and  $Co_4O_3(NH_3)_6(C_2O_4)_3.10H_2O$ ; and A. Werner's *oxo-trimido-salts*,  $[Co_4(O_2)_2(NH_3)_3(NO_3)_5]$ , and with Cl or Br in place of the nitrate-radicle; A. Werner and R. Feenstra's *imido-compounds*,  $Co_2(NH_3)_8py_3(NH)Cl_4$ , and the corresponding iodide, as well as A. Werner and F. Steinitzer's  $Co_2(NH_3)_6(NH)Br_4$ , as well as the corresponding iodide. E. Frémy, C. D. Braun, and G. Vortmann reported the *cobaltic fusco-salts*,  $Co_2(NH_3)_5(OH)_4(NO_3)_2$ ;  $Co_2(NH_3)_8(OH)_2(NO_3)_4.2H_2O$ ;  $Co_2(NH_3)_8(OH)_2Cl_4.2H_2O$ ;  $Co_2(NH_3)_2(OH)_2(SO_4)_2.3H_2O$ ;  $Co_2(NH_3)_6(SO_4)_3.6H_2O$ ;  $Co_2(NH_3)_6(OH)_2(CO_3)_2.3H_2O$ ; and the  $Co_2(NH_3)_2(SO_3)_3.5H_2O$ , and  $Co_2(NH_3)_5(SO_3)_3.7H_2O$  of K. A. Hofmann and S. Reinsch. There are K. A. Hofmann's *sulpho-salts* and *thiocarbonates*:  $Co_2(CS_3)_2S(NH_3)_4$ .

$2\text{H}_2\text{O}$ ;  $\text{Co}_2(\text{CS}_3)_2\text{S}_2(\text{NH}_3)_5$ ;  $\text{Co}_2(\text{CS}_3)_2\text{S}_2(\text{NH}_3)_5\cdot\text{H}_2\text{O}$ ; and  $\text{Co}_2(\text{CS}_3)_3\text{S}(\text{NH}_3)_2(\text{CH}_3\text{COOH})\cdot 4\text{H}_2\text{O}$ . The following mixed salts were reported by G. Vortmann and O. Blasberg, or by G. Vortmann and G. Magdeburg:  $\text{Co}(\text{NH}_3)_4\text{Cl}_2\cdot\text{I}\cdot\text{H}_2\text{O}$ ;  $\text{Co}(\text{NH}_3)_4(\text{SO}_3)\text{Cl}\cdot 2\text{H}_2\text{O}$ ;  $\text{Co}(\text{NH}_3)_4(\text{SO}_4)\text{Br}$ ;  $\text{Co}(\text{NH}_3)_4(\text{SO}_4)\text{I}$ ; and  $\text{Co}(\text{NH}_3)_4(\text{NO}_3)\text{I}\cdot\text{H}_2\text{O}$ . J. Beato and M. de los D. Brugger obtained complexes with the cobaltic chloride and cyclicamines—dimethylglyoxime associated with aniline, or *o*- or *p*-toluidine. Similar complexes were not formed with benzaldioxime or formaldioxime in place of diacetyldioxime.

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## § 18. Cobaltous Bromide

According to J. B. Berthelot,<sup>1</sup> cobalt at a dull red-heat unites with bromine to form **cobaltous bromide**,  $\text{CoBr}_2$ , which fuses and is partially decomposed at a

higher temp. F. Ducelliez and A. Raynaud said that the action of bromine is perceptible above the b.p. In order to purify the salt, T. W. Richards and G. P. Baxter recommended subliming the product in a mixture of hydrogen bromide, and C. F. Rammelsberg, and W. N. Hartley said that the hydrates pass into the anhydrous salt when heated to 130°. J. Nicklés observed that cobalt is only slightly attacked by a soln. of bromine in ether; and F. Ducelliez and A. Raynaud observed that the salt  $\text{CoBr}_2 \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$  is formed, and when heated, the ether is given off, and anhydrous cobaltous bromide remains. F. Bourion heated cobalt oxide in a current of hydrogen bromide mixed with a little sulphur monochloride as in the case of the corresponding nickel salt. Black cobalt oxide was found by M. Barre to be attacked at ordinary temp. by sulphur monobromide; the reaction is rapid at 350°; and at 700°, the product sublimes as a product of a high degree of purity—at 500°, 5 grms. of oxide were converted into the bromide in 1 hour. G. Crut found that dry hydrogen bromide converts anhydrous cobalt chloride into bromide at 500°; and A. Grün and E. Boedecker obtained the anhydrous bromide by heating the complex with pinacone over 100°. According to W. N. Hartley, I. Guareschi, and G. L. Clark and H. K. Buckner, the formation of the anhydrous bromide from the hydrate proceeds very slowly in vacuo over conc. sulphuric acid at ordinary temp. W. Biltz and B. Fetkenheuer recommended drying the hexahydrate in a desiccator over caustic alkali for some hours, then warming it to 40°, and finally dehydrating the salt at 140° to 160°. The rise of temp. must be slow to avoid melting the salt. W. N. Hartley, and A. Hantzsch and F. Schlegel recommended heating the hydrate to 130°; and I. Guareschi, to 100°. A. Ferrari and F. Giorgi heated the hydrate in a current of hydrogen bromide to avoid the formation of a basic salt.

J. B. Berthémot obtained a soln. of cobalt bromide by the action of a boiling mixture of water and bromine on cobalt; C. F. Rammelsberg added that the action is accelerated by contact with platinum. W. N. Hartley treated for a week at ordinary temp. a mixture of bromine with a little water, and evaporated the soln. in vacuo over sulphuric acid. The aq. soln. was also obtained by J. B. Berthémot by dissolving cobaltous hydroxide in hydrobromic acid; and by G. L. Clark and H. K. Buckner, by dissolving the carbonate in hydrobromic acid of sp. gr. 1.49. The evaporation of the aq. soln. furnishes purple-red or rose-red, prismatic crystals of the *hexahydrate*,  $\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$ , which, according to W. N. Hartley, at 100°, forms the reddish-violet *dihydrate*,  $\text{CoBr}_2 \cdot 2\text{H}_2\text{O}$ . I. Guareschi said that several intermediate hydrates are formed by heating the hexahydrate in dry air. A. Hantzsch and F. Schlegel, and I. Guareschi obtained the dihydrate by keeping the hexahydrate in vacuo over sulphuric acid or phosphorus pentoxide at ordinary temp. G. L. Clark and H. K. Buckner said that all the water is abstracted if the hexahydrate be kept in vacuo over sulphuric acid. I. Guareschi observed that the dihydrate passes into the blue *monohydrate*,  $\text{CoCl}_2 \cdot \text{H}_2\text{O}$ , at 80°; and A. Hantzsch and F. Schlegel, at 90°. I. Guareschi added that rose-coloured *hemihydrate*,  $\text{CoBr}_2 \cdot 5\frac{1}{2}\text{H}_2\text{O}$ ; pink *pentahydrate*,  $\text{CoBr}_2 \cdot 5\text{H}_2\text{O}$ ; reddish-violet *tetrahydrate*,  $\text{CoBr}_2 \cdot 4\text{H}_2\text{O}$ ; and the *hemihydrate*,  $\text{CoBr}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ , are formed during the dehydration of the hexahydrate, but it is very doubtful if these alleged hydrates are chemical individuals. A. Hantzsch and H. Carlsohn discussed the nature of this salt.

**Physical properties.**—The anhydrous bromide, left on dehydrating the hydrate, is a bright green powder; and the sublimed bromide appears in green, tabular crystals. The hexahydrate furnishes rose-red crystals; the dihydrate forms a purple-blue mass; and the monohydrate, a blue, hydrogropic mass. A. Ferrari and F. Giorgi found that the X-radiograms indicated that the space-lattice is of the cadmium iodide type. The space-lattice of the hexagonal crystals has  $a=3.685 \text{ \AA.}$ ,  $c=6.120 \text{ \AA.}$ , and  $a:c=1:1.66$ . The corresponding calculated sp. gr. is 5.072. G. L. Clark and H. K. Buckner observed 4.91 for the sp. gr. of the anhydrous salt. T. W. Richards and G. P. Baxter gave 4.909 at 25°/4°; and W. Biltz and E. Birk, 4.849 at 25°/4°; G. L. Clark and H. K. Buckner gave 2.46 for the sp. gr. of the hexahydrate at 25°/4°. A. Heydweiller gave for the sp. gr. of aq. soln., at 18°:

	4N-	3N-	2N-	N-	0.5N-	0.2N-	0.1N-
Sp. gr. .	1.3278	1.2474	1.1661	1.0837	1.04213	1.0170	0.00849
$\lambda$ .	33.22	41.3	51.3	63.8	72.8	81.7	87.7

W. Biltz and E. Birk gave 45.12 for the mol. vol. of the anhydrous salt. W. Biltz, I. I. Saslawsky, F. Ephraim, and F. Ephraim and O. Schütz discussed the mol. vol., and the contraction which attends the formation of the salt from its elements; and G. L. Clark and H. K. Buckner noted that there is a 18.58 per cent. contraction in forming the hexahydrate:  $\text{CoBr}_2 + 6\text{H}_2\text{O} = \text{CoBr}_2 \cdot 6\text{H}_2\text{O}$ . U. Panichi discussed the relation between the at. vol. of the contained elements and the sp. gr. of cobalt bromide. D. Isaachsen observed that the lowering of the f.p. of water, and the raising of the b.p. of water suggested that in aq. soln. cobalt bromide is present in the form of  $\text{CoBr}_2$ -mols.; A. Werner came to a similar conclusion with respect to the b.p. of pyridine soln.; and E. Beckmann, with respect to the b.p. of quinoline soln.

G. Devoto and A. Guzzi gave  $678^\circ$  for the m.p. of the anhydrous bromide in nitrogen; and A. Ferrari and F. Giorgi,  $687^\circ$  for the m.p. in hydrogen bromide. According to I. Guareschi, the hexahydrate melts at  $49^\circ$  to a blue liquid; and W. N. Hartley gave  $47^\circ$  to  $48^\circ$  for the m.p., and added that at  $100^\circ$ , the deep blue liquid gives off water to form the dihydrate, and at  $130^\circ$ , the anhydrous salt. D. Isaachsen measured the lowering of the f.p., and the raising of the b.p. of aq. soln., and the results agree with the formation of three ions:  $\text{CoBr}_2 \rightleftharpoons \text{Co}^{++} + 2\text{Br}^-$ . K. Jellinek and R. Ulroth gave for the dissociation press.  $p_{\text{Br}_2} = 4.07 \times 10^{-10}$  at  $500^\circ$ ;  $8.71 \times 10^{-9}$  at  $575^\circ$ ; and  $1.41 \times 10^{-7}$  at  $650^\circ$ . W. Biltz and E. Birk, and H. Fesefeldt noted that the salt sublimes when heated in vacuo. G. Crut gave for the heat of formation of the anhydrous bromide from gaseous bromine,  $(\text{Co}, \text{Br}_2) = 63.8$  Cals.; J. Thomsen gave  $(\text{Co}, \text{Br}_2, \text{Aq.}) = 72.94$  Cals.; M. Berthelot,  $(\text{Co}, \text{Br}_2, \text{Aq.}) = 13.4$  Cals. with liquid bromine, and 80.8 Cals. with gaseous bromine. G. Crut gave 18.4 Cals. for the heat of soln. of the anhydrous salt in water, and  $-1.28$  Cals. for the hexahydrate. G. Devoto and A. Guzzi calculated 28,940 Cals. for the free energy of formation of the molten salt. The subject was discussed by F. Ephraim.

R. W. Roberts measured the indices of refraction of soln. with 0.110 grm. of  $\text{CoBr}_2$  per c.c. of soln. (sp. gr. 1.100), for light of wave-length  $\lambda$ , and found 1.3520 for  $\lambda = 589.3m\mu$ , and 1.3704 for  $\lambda = 353.5m\mu$ . G. Limann made observations on the subject. A. Heydweiller measured the dispersion of the soln.; and G. Limann gave 26.03 for the mol. refraction for the D-line with the  $\mu^2$ -formula. H. Fesefeldt measured the absorption spectrum of thin films of anhydrous cobalt bromide, and observed bands between 250 and  $300m\mu$ . R. W. Roberts measured the magnetic rotation of the plane of polarized light and found it to be positive like that of the chloride. The colour, and absorption spectrum were studied by W. R. Brode, W. R. Brode and R. A. Morton, F. L. Cooper, G. Denigès, R. A. Houstoun and co-workers, R. J. Macwalter and S. Barratt, and H. C. Jones and co-workers.

A. Heydweiller's values for the eq. electrical conductivity of aq. soln. of an eq. of the salt, in  $v$  litres of water, at  $18^\circ$ , are indicated above. W. Althammer found for the mol. conductivity of soln. with a mol. of the salt, in  $v$  litres, at  $25^\circ$ :

$v$ .	20	80	320	1280	5120
$\mu$ .	99.5	110.0	118.6	124.0	127.4

L. G. Winston and H. C. Jones' values are:

	4	32	128	1024	2048	2096
$v$						
$\lambda$ $\left\{ \begin{array}{l} 0^\circ \\ 25^\circ \\ 35^\circ \end{array} \right.$	$\left\{ \begin{array}{l} 87.82 \\ 155.60 \\ 196.30 \end{array} \right.$	$\left\{ \begin{array}{l} 105.56 \\ 193.09 \\ 233.04 \end{array} \right.$	$\left\{ \begin{array}{l} 115.88 \\ 214.02 \\ 259.91 \end{array} \right.$	$\left\{ \begin{array}{l} 120.80 \\ 231.56 \\ 281.16 \end{array} \right.$	$\left\{ \begin{array}{l} 124.00 \\ 234.28 \\ 283.65 \end{array} \right.$	$\left\{ \begin{array}{l} 125.45 \\ 236.78 \\ 289.34 \end{array} \right.$
$\alpha$ $\left\{ \begin{array}{l} 0^\circ \\ 25^\circ \\ 35^\circ \end{array} \right.$	$\left\{ \begin{array}{l} 70.0 \\ 65.7 \\ 67.8 \end{array} \right.$	$\left\{ \begin{array}{l} 84.1 \\ 81.5 \\ 80.5 \end{array} \right.$	$\left\{ \begin{array}{l} 92.3 \\ 90.4 \\ 89.8 \end{array} \right.$	$\left\{ \begin{array}{l} 96.3 \\ 97.8 \\ 97.2 \end{array} \right.$	$\left\{ \begin{array}{l} 98.8 \\ 98.9 \\ 97.7 \end{array} \right.$	$\left\{ \begin{array}{l} 100.0 \\ 100.0 \\ 100.0 \end{array} \right.$

The values for the percentage ionizations,  $\alpha$ , were calculated from the conductivity data. Observations were also made by H. C. Jones and A. P. West, and H. C. Jones and W. W. Strong. A. Heydweiller gave for the limiting value at infinite dilution  $\lambda=111$  at  $18^\circ$ ; G. Bredig, 129.7 at  $25^\circ$ ; and W. Althammer, 128.9 at  $25^\circ$ . The effect of temp. was discussed by L. G. Winston and H. C. Jones, H. C. Jones and A. P. West, J. Hamacher, and D. Isaachsen. W. Althammer calculated the degree of hydrolysis of soln. with 0.05 and 0.01 mol per litre to be respectively 0.15 and 0.62, at  $25^\circ$ . W. Althammer found the transport number of the anion in soln. with a mol. of the salt in  $v$  litres, at  $18^\circ$ : 0.6088 for  $v=52.41$ , and 0.6045 for  $v=197.6$ ; and for the cation, with soln. containing  $C$  mol of the salt per litre, at  $25^\circ$ :

$C$ .	.	.	0.090	0.459	1.345	3.106	4.731	5.554
$n$ .	.	.	0.409	0.413	0.340	0.215	0.005	-0.444

$n$  is constant in dil. soln., and the decrease which occurs with increasing concentration is attributed to the formation of complex salts. P. B. Davis and co-workers measured the conductivity of soln. in formamide.

G. Devoto and A. Guzzi found the decomposition potential of fused cobalt bromide to be 0.680 volt at  $700^\circ$ , 0.534 volt at  $800^\circ$ , and 0.398 volt at  $900^\circ$ . W. Althammer gave for the e.m.f. of the cell (pt) $H_2$  |  $CoBr_2$  |  $KCl_{sat. soln.}$  | 0.1N-KCl,  $Hg_2Cl_2$  | Hg, 0.576 and 0.578 volt, respectively, for soln. of cobalt bromide with 0.05 and 0.01 mol per litre. G. Tammann and H. O. von Samson-Himmelsjerna studied the potential of cobalt in soln. of the bromide; and H. N. Holmes, the electrostenolysis of soln. of the salt.

W. Klemm and W. Schüth found that the magnetic susceptibilities of cobaltous bromide at  $91^\circ K.$ ,  $195^\circ K.$ ,  $293^\circ K.$ , and  $513^\circ K.$ , were, respectively,  $\chi \times 10^6=187$ , 93.4, 61.0, and 32.0. A. Quartaroli found that conc. aq. soln. of cobalt bromide are paramagnetic, and that with dil. soln., the diamagnetic properties of the water dominate with concentrations below 3.81 grms. of cobalt per litre. O. Liebknecht and A. P. Wills gave  $47.3 \times 10^{-6}$  mass unit for the magnetic susceptibility of a soln. at  $18^\circ$ . C. Falkenberg and R. Oppermann, and R. Oppermann studied the subject.

**Chemical properties.**—For the reduction of cobalt bromide by **hydrogen**, *vide supra*, cobalt. F. de Carli compared the results with those of other metal halides. G. Crut observed that the reduction of cobalt bromide by hydrogen is a reversible process:  $CoBr_2 + H_2 \rightleftharpoons 2HBr + Co$ , and the equilibrium constant,  $K = p_{HBr}/p_{H_2}$ , was found by K. Jellinek and R. Ulroth to be 0.190 at  $500^\circ$ , 0.485 at  $575^\circ$ , and 1.35 at  $650^\circ$ . G. Crut observed the press.,  $p$  mm., of the gas phase, and the vol. per cent. of HBr, in the gas phase to be:

445°			576°		
$p$ .	.	.	706	483.3	243.5
HBr	.	.	50.9	58.9	71.7
	656.1	333.5			
	8.7	13.13			
		145.5			
		18.16			

The chemical constant of the reaction is 11.87, and the heat of the reaction is 39.2 Cals. at  $15^\circ$ . I. Guareschi, and M. Barre said that on exposing anhydrous cobalt bromide to **air**, the dihydrate is formed, and C. F. Rammelsberg, and T. W. Richards and G. P. Baxter, that with a prolonged exposure, the hexahydrate is formed. J. B. Berthemot, and C. F. Rammelsberg also said that the hexahydrate deliquesces in air, forming a red liquid, but in dry air, efflorescence occurs. I. Guareschi, and H. Schulze showed that when heated in air, cobalt bromide gives off bromine, and forms the oxide. T. W. Richards and G. P. Baxter observed that when heated in **oxygen**, cobalt bromide is more readily attacked than is the case with nickel bromide; and similarly with **water** vapour. J. B. Berthemot, and T. W. Richards and G. P. Baxter observed that the salt is readily dissolved by cold water. A. Étard gave for the percentage solubility: 66.7 at  $59^\circ$ , 66.8 at  $75^\circ$ , and 68.1 at  $97^\circ$ . P. Job studied the constitution of **hydrobromic acid** soln. of the bromide, and obtained indications of the ions  $CoBr^+$ , and  $CoBr_3^-$ . C. Dufraise and D. Nakae

studied the catalytic effect on the oxidation of soln. of **sodium sulphite**; A. Hantzsch and H. Carlsohn, the reaction with dil. **sulphuric acid**; and P. Walden, the solubility of the salt in **chlorosulphonic acid**.

C. F. Rammelsberg showed that dry cobaltous bromide absorbs dry **ammonia**, becoming first red, and then forming brownish-red **cobaltous hexamminobromide**,  $\text{CoBr}_2 \cdot 6\text{NH}_3$ . The salt was also prepared by F. Ephraim in this manner. C. F. Rammelsberg added that the complex salt loses ammonia when it is heated; with water it forms green flecks of bromiferous hydroxide, and a brown ammoniacal liquid. W. Biltz and B. Fetkenheuer obtained it by treating a hot, conc., aq. soln. of the bromide with conc. aq. ammonia until the precipitate passes into soln., then adding air-free alcohol until a turbidity appears, and then cooling. The precipitated hexammine can be washed with alcohol. A. Naumann and J. Rill obtained the hexammine, in rose-red crystals, by passing ammonia gas into a soln. of cobaltous bromide in methyl acetate. W. Biltz observed no evidence of the formation of a decammine, analogous to the cobaltous decamminochloride (*q.v.*), which is formed at approximately  $-78^\circ$ . W. Biltz and E. Birk gave  $10.42 \text{ A.}$  for the lattice parameter (*vide supra*, the chloride); and G. B. Naess and O. Hassel,  $a=10.39 \text{ A.}$ , and  $4.50 \text{ A.}$  for the distance between the Co and Br atoms. The sp. gr. of the rose-red crystals of the hexammines prepared by the wet process, was found by W. Biltz and E. Birk to be  $1.871$  at  $25^\circ/4^\circ$ , and the mol. vol.  $171.6$ ; they gave  $1.879$  for the sp. gr. of the salt prepared by the dry process; and G. L. Clarke and H. K. Buckner gave  $1.955$ . The mol. vol. of the contained ammonia was discussed by W. Biltz. The dissociation temp. for  $p=100 \text{ mm.}$  was found by W. Biltz and G. F. Hüttig to be  $121^\circ$ ; and F. Ephraim found the dissociation press.,  $p \text{ mm.}$ , at different temp. to be:

	$104^\circ$	$121.5^\circ$	$142^\circ$	$159.5^\circ$	$170.5^\circ$	$175^\circ$	$176.5^\circ$
$p$	74	110	207	405	590	684	728

The results are plotted in Fig. 113. Observations were also made by W. Peters. W. Biltz and B. Fetkenheuer obtained rather larger values than did F. Ephraim; at  $136.8^\circ$ , they observed  $p=200 \text{ mm.}$  in place of F. Ephraim's  $177 \text{ mm.}$  W. Biltz and B. Fetkenheuer found it melts with decomposition at  $258^\circ$ . The heat of formation from cobaltous bromide and ammonia was found by W. Biltz and co-workers to be  $16.19 \text{ Cals. per mol. of } \text{NH}_3$ ; and from  $\text{CoBr}_2 \cdot 2\text{NH}_3$ ,  $14 \text{ Cals. per mol. of } \text{NH}_3$ . G. Beck gave  $452 \text{ Cals.}$  for the heat of formation. The subject was discussed by G. L. Clark, and W. Hieber and E. Levy. W. R. Brode and R. A. Morton examined the spectra of soln. of cobalt bromide in hydrobromic acid.

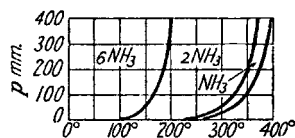


FIG. 113.—Dissociation Pressure of the Cobaltous Amminobromides.

A. Naumann and J. B. Kämmerer observed that if ammonia be passed into a half-sat. soln. of cobaltous bromide in benzonitrile, the blue precipitate which is formed turns rose-red, and its composition corresponds with **cobaltous tetramminobromide**,  $\text{CoBr}_2 \cdot 4\text{NH}_3$ . It is soluble in dil. acids, but only attacked with difficulty by conc. hydrochloric and nitric acids. The thermal dissociation of the hexammine gives no evidence of the formation of the tetrammine, since the reaction can be symbolized,  $\text{CoBr}_2 \cdot 6\text{NH}_3 \rightleftharpoons \text{CoBr}_2 \cdot 2\text{NH}_3 + 4\text{NH}_3$ . W. Biltz and B. Fetkenheuer observed that the hexammine passes into **cobaltous diamminobromide**,  $\text{CoBr}_2 \cdot 2\text{NH}_3$ , at  $136^\circ$ . A. Naumann and J. Rill prepared a diammine by heating the hexammine to  $120^\circ$ , and, as in the case of the  $\beta$ -diamminochloride (*q.v.*), the product is called *stable* or  $\alpha$ -form, or the *cis*-form, the other bluish-violet variety is the *unstable* or  $\beta$ -form, or the *trans*-form. W. Biltz, and W. Biltz and B. Fetkenheuer observed that there is complete series of solid soln. between the hexammine and the diammine, as in the analogous case of the aminochlorides (*q.v.*). The dissociation press. of the diammine is  $0.43 \text{ mm.}$  at  $152.4^\circ$ ;  $0.695 \text{ mm.}$  at  $160.5^\circ$ ;  $2.04 \text{ mm.}$

at  $181.8^{\circ}$ ; and 100 mm. at  $279^{\circ}$ —*vide* Fig. 113. W. Hieber and E. Levy studied the energy of formation of the diammine; and W. Klemm and W. Schüth, the magnetic susceptibilities. The diammine dissociates to furnish **cobaltous monamminobromide**,  $\text{CoBr}_2 \cdot \text{NH}_3$ . The heat of formation of the diammine is 20.58 Cals. per mol. of  $\text{NH}_3$ . The m.p. is  $260^{\circ}$ . W. Biltz and B. Fetkenheuer obtained the monammine by heating the diammine to  $181.8^{\circ}$ , or, according to G. L. Clark and H. K. Buckner, by heating a mixture of the theoretical proportions of cobaltous bromide and its hexammine, in a sealed tube, at  $230^{\circ}$ . W. Biltz, and W. Biltz and B. Fetkenheuer observed that at  $161.4^{\circ}$ ,  $181.8^{\circ}$ ,  $188.6^{\circ}$ , and  $208.4^{\circ}$  the respective dissociation press. are: 0.29, 0.99, 1.22, and 3.46 mm., and at  $297^{\circ}$ , 100 mm.—*vide* Fig. 113. The product of the dissociation is anhydrous cobaltous bromide. According to W. Biltz and co-workers, the heat of formation of the monammine is 21.1 Cals.

H. Franzen and O. von Mayer prepared **cobaltous dihydrazinodibromide**,  $\text{CoBr}_2 \cdot 2\text{N}_2\text{H}_4$ , by shaking 5 grms. of cobaltic bromopentamminobromide with 50 c.c. of a 50 per cent. soln. of hydrazine hydrate. When the evolution of ammonia has ceased, the mixture is heated on a water-bath, and on cooling, the salt is deposited as a violet powder. The salt is decomposed by boiling water; and when heated in a current of carbon dioxide, the hydrazine is expelled. W. Hieber and co-workers studied the energy of formation. A. Ferratini reported that **cobaltous hemipentamminodibromide**,  $\text{CoBr}_2 \cdot 2\text{N}_2\text{H}_4 \cdot \frac{1}{2}\text{N}_2\text{H}_4$ , is formed by aq. soln. of the components, and boiling the product with 94 per cent. alcohol. The dark violet powder melts between  $200^{\circ}$  and  $213^{\circ}$ ; it is readily soluble in water; and decomposed by alcohol. P. Walden observed that cobaltous bromide is very sparingly soluble in **arsenic trihydride**; B. A. Isbekoff and W. Plotnikoff found that it forms a homogeneous, bluish-green mass with molten **aluminium bromide**, and that the sp. conductivity of the soln. at  $150^{\circ}$  is 0.0008 mho.

I. Guareschi noted that cobalt bromide is slightly soluble in dry **chloroform**; and that it is soluble in **methyl alcohol**; and E. Lloyd and co-workers gave for the solubility,  $S$  grm. of  $\text{CoBr}_2$  per gram of methyl alcohol:

$S$	$20^{\circ}$ 0.430	$30^{\circ}$ 0.586	$35^{\circ}$ 0.800	$40^{\circ}$ 1.248	$50^{\circ}$ 1.419	$60^{\circ}$ 1.531	$70^{\circ}$ 1.690	$80^{\circ}$ 1.906
	$\text{CoBr}_2 \cdot 6\text{CH}_3\text{OH}$			$\text{CoBr}_2 \cdot 3\text{CH}_3\text{OH}$			$\text{CoBr}_2 \cdot 2\text{CH}_3\text{OH}$	

Observations of the complex  $\text{CoBr}_2 \cdot 6\text{CH}_3\text{OH}$  were made by A. Hantzsch and F. Schlegel; E. Lloyd and co-workers found the partial press. at  $10^{\circ}$ ,  $20^{\circ}$ , and  $30^{\circ}$  to be, respectively, 14.4, 31.0, and 64.1 mm. E. Lloyd and co-workers found the partial press. of the complex  $\text{CoBr}_2 \cdot 3\text{CH}_3\text{OH}$  to be 17 mm. at  $20^{\circ}$ , and of the complex  $\text{CoBr}_2 \cdot 2\text{CH}_3\text{OH}$ , 10 mm. The latter complex was also studied by A. Hantzsch and F. Schlegel. The colour and absorption spectrum of the soln. were studied by F. L. Cooper, A. Hantzsch, and H. C. Jones and J. A. Anderson; and the mol. conductivity by H. R. Kreider and H. C. Jones. E. Lloyd and co-workers found the solubility,  $S$  grm. of  $\text{CoBr}_2$  per gram of **ethyl alcohol**, to be:

$S$	$10^{\circ}$ 0.706	$20^{\circ}$ 0.771	$30^{\circ}$ 0.849	$40^{\circ}$ 0.959	$50^{\circ}$ 1.050	$60^{\circ}$ 1.208	$65^{\circ}$ —	$70^{\circ}$ 1.271	$80^{\circ}$ 1.294
	$\text{CoBr}_2 \cdot 3\text{C}_2\text{H}_5\text{OH}$					$\text{CoBr}_2 \cdot 2\text{C}_2\text{H}_5\text{OH}$			

The partial pressure of  $\text{CoBr}_2 \cdot 3\text{C}_2\text{H}_5\text{OH}$  is 1.51, 10.5, and 50.6 mm., respectively, at  $10^{\circ}$ ,  $30^{\circ}$ , and  $50^{\circ}$ ; and 2 mm. at  $20^{\circ}$  for  $\text{CoBr}_2 \cdot 2\text{C}_2\text{H}_5\text{OH}$ . A. Hantzsch and F. Schlegel obtained  $\text{CoBr}_2 \cdot 2\text{C}_2\text{H}_5\text{OH}$  by concentrating the alcoholic soln. over phosphorus pentoxide. The colour and absorption spectrum of the soln. were studied by W. R. Brode, F. L. Cooper, R. A. Houstoun and A. R. Brown, R. A. Houstoun and A. H. Gray, and H. C. Jones and J. A. Anderson; the mol. conductivity, by H. R. Kreider and H. C. Jones; and the transport number, by H. G. Denham. Alcoholic sulphuric acid was found by A. Hantzsch and H. Carlsohn immediately to

decompose the alcoholic soln. of cobalt bromide. A. Hantzsch discussed the colour of the soln. in **amyl alcohol**; and A. Hantzsch and F. Schlegel, the colour of soln. in **benzyl alcohol**, and also the formation of a complex salt. A. Hantzsch discussed the colour of soln. in **ethylene glycol**; and A. Grün and E. Boedecker observed the formation of the complex salts,  $\text{CoBr}_2 \cdot 3\text{C}_2\text{H}_4(\text{OH})_2$ , and  $\text{CoBr}_2 \cdot 2\text{C}_2\text{H}_4(\text{OH})_2$ . A. Grün and E. Boedecker also observed a complex salt is formed with **pinacone**,  $\text{CoBr}_2 \cdot 3\text{C}_6\text{H}_{12}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ . A. Hantzsch found that **glycerol** forms a rose-red soln. at ordinary temp.; H. C. Jones and W. W. Strong studied the absorption spectrum; and H. C. Jones and J. S. Guy, the mol. conductivity. P. Walden measured the conductivity of soln. in **acetaldehyde**, and in **benzaldehyde**. C. Dufraisse and D. Nakae studied the catalytic action of cobalt bromide on the oxidation of **acraldehyde**, **phenylaldehyde**, **furfuraldehyde**, **styrene**, and **turpentine**. I. Guareschi noted the solubility of the bromide in **methylethylketone**. A. Hantzsch studied the colour of soln. of cobalt bromide in **ether**; and F. Ducelliez and A. Raynaud, the complex  $\text{CoBr}_2 \cdot (\text{C}_2\text{H}_5)_2\text{O}$ . W. Eidmann, A. Hantzsch and H. Carlsolm, A. Naumann, and I. Guareschi studied the colour of soln. in **acetone**. The solubility,  $\text{S}$  grm. of  $\text{CoBr}_2$  per gram of acetone, was found by W. R. G. Bell and co-workers to be:

	0°	10°	15°	30°	40°
<i>S</i> . . .	0.541	0.543	0.650	0.696	0.924

when the solid phase is  $\text{CoBr}_2 \cdot \text{C}_3\text{H}_6\text{O}$ , the partial press. at 10°, 20°, and 30° are, respectively, 4.0, 11.7, and 25.2 mm. I. Guareschi studied the complex with **acetophenone**, namely,  $\text{CoBr}_2 \cdot \text{CH}_3 \cdot \text{CO} \cdot \text{C}_6\text{H}_5$ .

I. Guareschi found that the bromide forms a bluish-violet soln. with **formic acid**, and P. Walden measured the conductivity of soln. in **acetic anhydride**. According to A. Naumann, one gram of cobalt bromide dissolves in 9.74 grms. of **methyl acetate**, at 18°, to form a soln. of sp. gr. 1.013 at 18°/4°; and the salt is sparingly soluble in **ethyl acetate**—A. Hantzsch studied the absorption spectrum of the soln.; and J. Schröder and H. Steiner, the raising of the b.p. A. Naumann and J. Rill said that hydrogen sulphide produces a slight turbidity with the soln., and ammonium sulphide precipitates cobalt sulphide quantitatively. P. Walden measured the conductivity of soln. in **cyanoacetic ether**, in **methyl thiocyanate**, and in **dimethyl malonate**. R. Fosse studied the complex formed with **dinaphthopyryliumbromide**.

P. Walden said that cold soln. of cobalt bromide in **formamide** are red, and that hot soln. are blue; I. Guareschi said that both hot and cold soln. are blue. P. B. Davis and co-workers measured the viscosity, mol. conductivity, and the degree of ionization of soln. at different temp. When the soln. is heated with mercuric chloride, mercury and anhydrous cobalt chloride are formed. A. Naumann observed that warm acetonitrile dissolves cobalt bromide, and A. Hantzsch obtained a complex,  $\text{CoBr}_2 \cdot 2\text{CH}_3\text{CN}$ , from a soln. of cobalt bromide in warm **acetonitrile**; P. Walden noted the electrical conductivity of the soln. A. Hantzsch obtained a complex with **isopropionitrile**, or **carbylamine**. F. Schlegel studied the complex with diacetonitrile. A. Naumann and J. B. Kämmerer observed that cobalt bromide readily dissolves in **benzonitrile**, forming a deep blue soln. which furnishes  $\text{CoBr}_2 \cdot 2\text{C}_6\text{H}_5\text{CN}$ , and if air is present,  $\text{CoBr}_2 \cdot 2\text{C}_6\text{H}_5\text{CN} \cdot 6\text{H}_2\text{O}$ . The colour of the soln. becomes red when silver nitrate, mercuric chloride, or cadmium iodide is added; lithium iodide makes the soln. apple-green; chlorine produces cobalt chloride; hydrogen sulphide yields a small precipitate; and ammonium sulphide precipitates cobalt sulphide quantitatively. Double salts are formed with cadmium iodide, and mercuric chloride.

F. Ephraim and R. Linn studied the complex salts with **methylamine**,  $\text{CoBr}_2 \cdot 6\text{CH}_3\text{NH}_2$ ; and W. Hieber and co-workers studied the stability of the complex. Similar remarks apply to the complex with **ethylamine**. G. Barbieri and F. Calzolari, and G. Scagliarini and G. Tartarini investigated the complexes formed with **hexamethylenetetramine** or **urotropin**; J. Moitessier, and W. Hieber



and co-workers, the complexes with **phenylhydrazine**; W. Hieber and co-workers, with **ethylenediamine**; J. Frejka and L. Zahlova, with **diaminobutene**; W. Hieber and co-workers, and R. Cernatescu and co-workers, the complex with **phenylenediamine**; G. Spacu, the complex with **benzidine**; and with **toluidine**; W. Hieber and co-workers, the formation of a complex with **aniline**; W. Hieber and F. Leutert, the complex with **acetaldoxime**, with **benzaldoxime**, and with **acetoxime**; and F. Feigl and H. Rubinstein, the complexes with **dimethylglyoxime**. A. Werner and W. Schmujlow found that cobaltous bromide is soluble in **pyridine**; W. R. Brode said that the soln. is rose-red at ordinary temp. and blue when heated. W. R. Brode studied the absorption spectrum, and P. Walden, the mol. conductivity; H. Grossmann, W. Biltz, W. Biltz and B. Fetkenheuer, R. Weinland and co-workers, W. Hieber and co-workers, and A. Hantzsch studied the complexes formed with pyridine; E. G. V. Percival and W. Wardlaw, the complexes with **quinaldine**; and F. Blau, the complexes with **dipyridyl**. E. Beckmann found that cobalt bromide is soluble in **quinoline**, the soln. is rose-red at ordinary temp., and blue when heated. W. R. Brode studied the absorption spectrum, and P. Walden, the mol. conductivity. H. Grossmann and F. Hünslers studied the complex formed with quinoline; F. Blau, the complex formed with **phenanthroline**; and M. R. Menz, the complexes formed with **camphidine**.

G. F. Campbell prepared **caesium cobaltous tetrabromide**,  $\text{Cs}_2\text{CoBr}_4$ , from soln. of the component salts with  $\text{Cs}:\text{Co}=1:1$  up to a high proportion of the cobalt salt; and **caesium cobaltous pentabromide**,  $\text{Cs}_3\text{CoBr}_5$ , from soln. of the component salts with  $\text{Cs}:\text{Co}=2:1$  up to  $1:1$ . The bromides resemble the chlorides. H. Franzen and H. L. Lucking obtained **hydrazonium cobaltous tetrabromide**,  $\text{CoBr}_2(\text{N}_2\text{H}_4\cdot\text{HBr})_2\cdot 4\text{H}_2\text{O}$ , by mixing soln. of cobaltous bromide and hydrazine bromide. A. Mailhe observed that **copper cobaltous trioxydibromide**,  $3\text{CuO}\cdot\text{CoBr}_2\cdot 4\text{H}_2\text{O}$ , or, according to A. Werner,  $\text{Cu}_2(\text{OH})_4\text{Cu}=(\text{OH}_2\cdots\text{Co}_2\cdot\text{H}_2\text{O})$ , is formed in green hexagonal plates, by the action of a soln. of cobalt bromide on copper hydroxide. H. C. Jones and co-workers measured the f.p., the absorption spectrum, and the electrical conductivity of some soln. of calcium and cobalt bromides, and of calcium bromide and cobalt chloride. R. Varet found that with **mercuric cobaltous bromide**, the heat of formation of  $\text{CoBr}_2\cdot 2\text{HgBr}_2$  is 3.09 Cals., and of  $\text{CoBr}_2\cdot\text{HgBr}_2$ , 2.84 Cals. F. Calzolari and U. Tagliavini obtained a complex with hexamethylenetetramine. A. Mailhe obtained **mercuric cobaltous oxybromide**,  $6\text{CoO}\cdot\text{CoBr}_2\cdot\text{HgBr}_2\cdot 20\text{H}_2\text{O}$ , as a green powder, by the action of a soln. of cobalt bromide on mercuric oxide. B. Rayman and K. Preis prepared **cobaltous stannic hexabromide**,  $\text{CoSnBr}_6\cdot 10\text{H}_2\text{O}$ —or, according to G. Spacu and J. Dick,  $[\text{Co}(\text{H}_2\text{O})_6][\text{SnBr}_6]\cdot 4\text{H}_2\text{O}$ —in yellowish-green, tabular crystals, by treating a conc. soln. of a cobaltous salt with bromostannic acid. G. Spacu and J. Dick observed complex salts are formed with diethylenediamine piperazine; with hexamethylenetetramine, or urotropine; with benzidine; and with pyridine.

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### § 19. Cobaltic Bromide and its Complex Salts

The preparation of **cobaltic bromide**,  $\text{CoBr}_3$ , as a chemical individual has not been achieved, yet, as in the case of the cobaltic salts generally, it is remarkable what an extensive variety of stable cobaltic salts can be obtained when the cobalt is associated with other radicles, etc. The general plan of description adopted in the case of the compounds of cobaltic chloride will here be followed, but, since the modes of preparation and several properties are usually similar to those of the corresponding chlorides, many details can be referred back to cobaltic aminochlorides.

#### *The $\text{CoA}_6$ or Hexammine Family.*

In 1857, F. A. Genth<sup>1</sup> described some properties of **cobaltic hexamminobromide**,  $[\text{Co}(\text{NH}_3)_6]\text{Br}_3$ ; and S. M. Jørgensen prepared this salt by the action of hydrobromic acid on cobaltic hexamminohydroxide. W. Biltz obtained this salt by adding hydrobromic acid to a hot, half-sat. soln. of the hexamminochloride. The rhombic, wine-yellow crystals were also prepared by A. B. Lamb and A. T. Larson. G. Bödtker-Naess and O. Hassel studied the lattice structure. W. Biltz and E. Birk gave 2.340 for the sp. gr. at  $25^\circ/4^\circ$ , and 171.3 for the mol. vol., and W. Biltz calculated that the mol. vol. of the  $\text{NH}_3$ -groups is 18 when that in the corresponding cobaltous salt is 21. The subject was discussed by E. Birk, R. Klement, and F. Ephraim and O. Schütz. W. Biltz observed no marked change in the hexamminobromide at  $216^\circ$ . A. Gordienko, A. N. Nikolopulos, R. Luther and A. N. Nikolopulos, and J. Lifschitz and E.<sup>1</sup> Rosenbohm studied the absorption spectrum. A. Werner and A. Miolati observed that the mol. conductivity,  $\mu$ , of soln. with a mol of the salt in  $v$  litres, at  $25^\circ$ , is:

$v$	.	.	.	125	250	500	1000	2000
$\mu$	.	.	.	343.8	378.0	401.0	426.9	442.2

and A. B. Lamb and V. Yngve gave for the mol. conductivity and degree of ionization,  $\alpha$ , of soln. with  $C$  mols per litre:

	$0^\circ$				$25^\circ$			
$C \times 10^3$	33.23	6.662	1.336	0.2678	33.23	6.662	1.336	0.2678
$\mu$	174.1	215.3	253.7	272.1	219.1	397.0	461.9	502.5
$\alpha$	58.6	72.5	85.4	91.6	57.6	77.1	83.4	90.6

The limiting value of  $\mu = 297.1$  at  $0^\circ$ , and 553.0 at  $25^\circ$ . P. Pascal gave for the magnetic susceptibility,  $-0.322 \times 10^{-6}$  mass unit. E. Rosenbohm, L. C. Jackson, and W. Biltz also studied the magnetic properties of the salt. P. Mosimann, and F. Ephraim and co-workers found that at  $18^\circ$ , a sat. aq. soln. has 2.404 grms., or 0.040 mol per litre. S. M. Jørgensen observed that soln. of the bromide behave towards reagents very much like those of the chloride. According to F. Ephraim, the hexabromide in liquid ammonia at  $-20^\circ$ , or in gaseous ammonia at  $-21^\circ$ , forms cobaltic enneamminobromide,  $[\text{Co}(\text{NH}_3)_9]\text{Br}_3 \cdot 3\text{NH}_3$ , and this compound, at  $-3^\circ$ , forms cobaltic heptamminobromide,  $[\text{Co}(\text{NH}_3)_7]\text{Br}_3 \cdot \text{NH}_3$ , and this, at  $4.5^\circ$  to  $10^\circ$ , returns to the hexammine.

F. Ephraim and co-workers observed that the hexamminobromide forms with cadmium bromide **cadmium cobaltic hexamminohexabromide**,  $2[\text{Co}(\text{NH}_3)_6]\text{Br}_3 \cdot 3\text{CdBr}_2 \cdot 3\text{H}_2\text{O}$ , in yellowish-brown, thin plates which have a sp. gr. of 3.006 at  $25^\circ$ ; and a mol. vol. of 556.4. The sp. gr. of the anhydrous salt is 2.998 at  $25^\circ$ , and the mol. vol., 539.9. F. Ephraim and co-workers obtained **mercuric cobaltic hexamminopentabromide**,  $[\text{Co}(\text{NH}_3)_5]\text{Br}_3 \cdot \text{HgBr}_2$ , in rectangular plates of sp. gr. 3.365 at  $25^\circ$ , and mol. vol., 226.3; they also obtained **mercuric cobaltic hexammineenneabromide**,  $[\text{Co}(\text{NH}_3)_6]\text{Br}_3 \cdot 3\text{HgBr}_2$ , in pale brown needles. They also reported **lead cobaltic hexammineheptabromide**,  $[\text{Co}(\text{NH}_3)_6]\text{Br}_3 \cdot \text{PbBr}_2$ , in brown

needles of sp. gr. 2.762 at 25°/4°, and mol. vol., 278—but there is some doubt about the individuality of this substance; **lead cobaltic tris-hexamminotridecabromide**,  $3[\text{Co}(\text{NH}_3)_6]\text{Br}_3 \cdot 2\text{PbBr}_2$ , in orange-brown needles; **lead cobaltic hexamminohenabromide**,  $[\text{Co}(\text{NH}_3)_6]\text{Br}_3 \cdot 4\text{PbBr}_2 \cdot 2\text{H}_2\text{O}$ , in yellow plates; and **bismuth cobaltic hexamminohexabromide**,  $[\text{Co}(\text{NH}_3)_6]\text{Br}_3 \cdot \text{BiBr}_3$ , as a pale yellow, flocculent precipitate.

A. Werner and E. Berl, and E. Berl prepared **cobaltic hexahydroxylamine-bromide**,  $[\text{Co}(\text{NH}_2\text{OH})_6]\text{Br}_3$ , by the action of hydrobromic acid on the hexahydroxylaminohydrochloride. The crystals are a darker yellow than the corresponding chloride. C. S. Borzekowsky prepared the dextro- and lævo-forms of **cobaltic hydroxylaminebisethylenediamineamminobromide**,  $[\text{Co}(\text{NH}_3)(\text{NH}_2\text{OH})\text{en}_2]\text{Br}_3$ .

H. Grossmann and B. Schück,<sup>2</sup> and L. L. Lehrfeld prepared **cobaltic tris-ethylenediaminebromide**,  $[\text{Co en}_3]\text{Br}_3 \cdot 3\text{H}_2\text{O}$ , by the aerial oxidation of a soln. of cobaltous bromide in ethylenediamine. The product was thought to be a dihydrate, but this was not confirmed by A. Benrath and W. Kohlberg. A. Werner obtained it by the action of sodium bromide on a soln. of the corresponding chloride; A. Werner and M. Basyrin, by adding sodium bromide to a soln. of the dichlorobisethylenediaminechloride or nitrate in a 10 per cent. aq. soln. of ethylenediamine; and P. Pfeiffer and T. Gassmann, by warming a mol. of chloropentamminochloride with 3 mols. of monohydrated ethylenediamine, dissolving the product in water, and precipitating by the addition of hydrobromic acid. A. Werner recommended the following process:

Dissolve 10 grms. of cobalt chloride in 150 grms. of 10 per cent. ethylenediamine, and oxidize the salt by leading air through the soln. The brown soln. so obtained is acidified with hydrochloric acid, evaporated to crystallization, the crystals dissolved in water, and ammonium nitrate added to the soln., whereby trans-dichloro-diethylenediaminecobaltic nitrate is precipitated. After collecting this salt the filtrate is precipitated with sodium bromide, giving pure trisethylenediaminecobaltic bromide.

The brownish-red or orange-red hexagonal plates or short prisms were found by F. M. Jäger to be pseudo-ditrigonal, with the axial ratio  $a : c = 1 : 0.6794$ ; he added that the crystals are more probably monoclinic, and isomorphous with the corresponding chloride, but with a different cleavage. F. M. Jäger gave 1.845 for the sp. gr. at 25°/4°. A. Benrath and W. Kohlberg, and A. G. Berghman measured the vap. press. of the hydrated salt, and the results indicated that the salt is a trihydrate, and that no dihydrate is formed under these conditions—*vide infra*. H. Grossmann and B. Schück gave 271° for the m.p. A. Benrath and W. Kohlberg, and A. G. Berghman studied the vap. press. curves. M. Delépine and R. Charonnet obtained optically active salts. A. Gordienko, T. Inoue, J. Angerstein, W. F. Beyer, and J. Lifschitz and E. Rosenbohm studied the absorption spectrum; and L. C. Jackson, the magnetic properties. E. Rosenbohm gave  $-1202 \times 10^{-7}$  mass unit for the magnetic susceptibility. P. Pfeiffer and T. Gassmann observed that the salt is soluble in hot and cold water, and that an aq. soln., sat. at 10°, contains 4.33 per cent. of the anhydrous salt. T. Inoue inferred from the absorption spectrum of aq. soln. that in presence of mercuric salts, a mercuric cobaltic trisethylenediamine bromide is probably formed in soln.

According to A. Werner, a *dextro-salt*, and a *lævo-salt* can be prepared from either the bromide-tartrate or the chloride-tartrate by trituration with warm concentrated hydrobromic acid. The soln., after filtering, deposits large, hexagonal plates, which are probably an acid bromide; on re-crystallization from water, large, columnar crystals of the dextro-bromide,  $[\text{Co en}_3]\text{Br}_3 \cdot 2\text{H}_2\text{O}$ , are obtained. The lævo-bromide,  $[\text{Co en}_3]\text{Br}_3 \cdot 2\text{H}_2\text{O}$ , is prepared, in a similar manner, from the gel of lævo-bromide-tartrate or the lævo-chloride-tartrate, the sparingly-soluble, inactive, or racemic bromide remains undissolved. According to F. M. Jäger, the dextro-salt forms brownish-red, thick, prismatic crystals with well-developed faces, whilst the crystals of the lævo-salt are dodecahedrons. The axial ratio of the bipyramidal, tetragonal crystals is  $a : c = 1 : 0.8399$ ; and the sp. gr. is 1.971 at 25°/4°. J. Angerstein, and J. Lifschitz and E. Rosenbohm found that aq. soln. of the optically inactive form and the two active forms have the same absorption spectrum. The

sp. rotation of a 1 per cent. soln. was found by A. Werner to be  $[\alpha] = 117^\circ$  for the dextro-salt, and  $-115^\circ$  for the lævo-salt. Observations were also made by W. Kuhn and E. Bein, F. M. Jäger, A. P. Smirnof, and J. Lifschitz and E. Rosenbohm. The magnetic properties were examined by E. Rosenbohm, and L. C. Jackson. A. Werner said that the optically-active forms are more soluble than the inactive forms. G. and P. Spacu obtained **mercury cobaltic trisethylene-diaminebromide**,  $[\text{Co en}_3]\text{HgBr}_5$ .

P. Pfeiffer and T. Gassmann prepared **cobaltic trispropylenediaminebromide**,  $[\text{Co pn}_3]\text{Br}_3 \cdot \text{H}_2\text{O}$ , in small, yellow crystals, by adding hydrobromic acid to an aq. soln. of the corresponding chloride. A sat., aq. soln. at  $16^\circ$  contains 0.808 grm. per c.c. of the anhydrous bromide. The absorption spectra of aq. soln. were studied by J. Lifschitz and E. Rosenbohm. E. Rosenbohm gave  $-4.34 \times 10^{-7}$  mass unit for the magnetic susceptibility of the solid. The magnetic properties were also studied by L. C. Jackson. The dihydrated *dextro-salt* and the *lævo-salt* were prepared by A. P. Smirnof, and their optical properties studied by J. Lifschitz and E. Rosenbohm, J. Lifschitz, and L. Tschugaeff and W. Sokoloff. J. Frejka and L. Zahlova prepared **cobaltic tris-butylene-diaminebromide**,  $[\text{Co bn}_3]\text{Br}_3$ . G. and P. Spacu prepared complexes with hexamethylenetetramine,  $[\text{Co h}_6](\text{SnBr}_6)$ ; with pyridine,  $[\text{Co py}_6](\text{SnBr}_6)$ ; and with piperidine,  $[\text{Co pd}_3](\text{SnBr}_6) \cdot 6\text{H}_2\text{O}$ . G. Spacu and R. Ripon prepared some complex pyridine salts.

A. Werner and C. Kreutzer,<sup>3</sup> K. R. Lange, and A. Werner prepared **cobaltic bisethylenediaminediamminobromide**,  $[\text{Co}(\text{NH}_3)_2\text{en}_2]\text{Br}_3$ , by treating the corresponding iodide with freshly-precipitated silver oxide, and saturating the filtrate with hydrobromic acid. The orange crystals, unlike the corresponding trans-salt, are freely soluble in water. A. Werner and Y. Shibata separated the *dextro-salt*, and the *lævo-salt* from the corresponding camphor bromosulphonates. The yellow, acicular crystals are freely soluble in water. The sp. rotation of a 1 per cent. aq. soln. of the dextro-salt is  $[\alpha] = 37^\circ$ , and for the lævo-salt,  $[\alpha] = -37^\circ$ . A. Werner and co-workers also prepared **cobaltic trans-bisethylenediaminediamminobromide** by the action of liquid ammonia on the dichloro-bisethylenediaminechloride, and treating the soln. with sodium bromide; by treating a trans- $[\text{Co}(\text{NH}_3)_2\text{en}_2(\text{CNS})]$ -salt, or a trans- $[\text{Co en}_2(\text{CNS})_2]$ -salt with perhydrol, and afterwards with hydrobromic acid; or by the action of potassium bromide on the corresponding chloride. Y. Shibata measured the absorption spectrum.

W. Kuhn and K. Bein studied the absorption spectrum of **cobaltic trisphenylenediaminechloride**,  $[\text{Co pn}_3]\text{Br}_3$ . A. Werner and K. Dawe prepared **cobaltic bispropylenediaminediamminobromide**,  $[\text{Co}(\text{NH}_3)_2\text{pn}_2]\text{Br}_3 \cdot \text{H}_2\text{O}$ , in golden-yellow needles, by adding an excess of hydrobromic acid to a boiling, conc. soln. of the corresponding chloride. F. M. Jäger and H. B. Blumendal obtained **cobaltic ethylenediaminobis-cyclopentanediaminebromide**,  $[\text{Co en}(\text{C}_5\text{H}_{12}\text{N}_2)_2]\text{Br}_3 \cdot \text{H}_2\text{O}$ , by treating the iodide with sodium bromide. P. Pfeiffer and T. Gassmann, by heating the cis- or trans-dichlorobisethylenediaminechloride with monohydrated propylenediamine on a water-bath, and then adding conc. hydrobromic acid. E. Rosenbohm, and L. C. Jackson studied the magnetic properties. F. M. Jäger and H. B. Blumendal prepared **cobaltic bisethylenediamine-trans-cyclopentanediaminebromide**,  $[\text{Co en}_2(\text{C}_5\text{H}_{12}\text{N}_2)]\text{Br}_3 \cdot \text{H}_2\text{O}$ , by treating the corresponding chloride with sodium bromide. They also prepared the *dextro-salt*, and the *lævo-salt*, as well as **cobaltic bisethylenediamine-1-cyclopentanediaminebromide**,  $[\text{Co en}_2(1\text{-C}_5\text{H}_{12}\text{N}_2)]\text{Br}_3 \cdot 2\text{H}_2\text{O}$ , and the *dextro-salt*. M. F. Jäger prepared **cobaltic bisethylenediamine- $\alpha$ -phenanthroline bromide**,  $[\text{Co en}_2(\text{C}_{12}\text{H}_8\text{N}_2)]\text{Br}_3$ , by treating the corresponding iodide with silver bromide. W. Tupizina, R. Plischke, and W. A. Redeker prepared **cobaltic pyridinebisethylenediamineaminobromide**,  $[\text{Co}(\text{NH}_3)_2\text{en}_2\text{py}]\text{Br}_3$ . C. J. Dippel and F. M. Jäger prepared **cobaltic trisdiaminopentanebromide**,  $[\text{Co ptn}_3]\text{Br}_3$ ; and **cobaltic bisethylenediaminodiaminepentane**,  $[\text{Co en}_2\text{ptn}]\text{Br}_3$ , with  $\alpha\beta$ - and  $\beta\beta$ -diaminopentane. G. Spacu and J. Dick prepared **cobaltic quinquesbenzidinopyridinohydroxybromostannate**,  $[\text{Co bzd}_5\text{py}][\text{SnBr}_6(\text{OH})]5\text{H}_2\text{O}$ ; J. C. Duff, **cobaltic succinatobisethylenediaminobromide**.

S. M. Jörgensen<sup>4</sup> prepared **cobaltic roseobromide**, or **cobaltic aquopentamminobromide**,  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Br}_3$ , by adding hydrobromic acid to an aq. or ammoniacal soln. of the nitrate; and A. Werner, by slowly adding hydrobromic acid to a boiling ammoniacal soln. of chloropentamminochloride, and then alcohol. The flesh-red powder is washed with alcohol and ether. The red octahedra, or rhombic plates were found by F. Ephraim and O. Schütz to have a sp. gr. of 2.269 at  $25^\circ$ , and a mol. vol., 177.1, corresponding with a vol. contraction of 59.2 per cent. during its formation. A. B. Lamb and J. W. Marden found the vap. press. at  $25^\circ$  is about 4 mm. The salt may be kept a long time, but S. M. Jörgensen found that it loses water rapidly at  $100^\circ$ , and forms bromopentamminobromide. A. B. Lamb and J. P. Simmons calculated  $-9.22$  Cals. for the mol. heat of solution at  $25^\circ$ . The

lowering of the f.p. of aq. soln. was studied by J. Petersen; the absorption spectrum, by A. N. Nikolopoulos, R. Luther and A. N. Nikolopoulos, and J. Angerstein. A. Werner and A. Miolati gave for the mol. conductivity,  $\mu$ , of soln. of a mol of the salt in  $v$  litres, at 25°:

$v$	125	250	550	1000	2000
$\mu$	333.6	365.4	390.3	412.9	436.4

Measurements were also made by Y. Shibata. J. Petersen calculated the degrees of ionization,  $\alpha$ , of the salt, from the eq. conductivity of soln. with 4, 50, and 1000 gram-equivalents per litre, at 18°, to be, respectively,  $\alpha=0.58, 0.82$ , and  $0.98$ . The polarization tension was studied by N. R. Dhar and G. Urbain—*vide supra*, the hexamminochloride. F. Ephraim observed that a sat., aq. soln. at 17.5° contains 0.364 mol per litre. A. B. Lamb and J. W. Marden found that a 0.01302*M*-soln. of aquopentamminobromide or bromopentamminobromide in 0.02*M*-HBr, contains after 30 hrs' heating at 70°, 98 per cent. of aquopentamminobromide, no matter which salt was employed at the start. F. Ephraim observed that ammonia acts on the bromide at -21°, forming a bluish-red **cobaltic aquopentadecamminobromide**,  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Br}_3 \cdot 10\text{NH}_3$ , and when heated to 21°, a series of solid soln. is formed until, at the limit, **cobaltic aquooctamminobromide**,  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Br}_2 \cdot 3\text{NH}_3$ , is produced, and this product is stable up to 90°. The solid soln. at 8° has the composition:  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Br}_3 \cdot 8\text{NH}_3$ . For the chemical reactions, *vide supra*, the corresponding chloride. Some double salts have been reported.

F. Ephraim and P. Mosimann were unable to prepare **zinc cobaltic aquopentamminobromide**, but they obtained **cadmium cobaltic aquopentamminobromide**,  $2[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Br}_3 \cdot 3\text{CdBr}_2$ , easily soluble in water. The dark red, tabular crystals of the sat. soln. were found by F. Ephraim and O. Schütz to have a sp. gr. of 2.961 at 25°, and a mol. vol. of 547.3, corresponding with a vol. contraction of 48.8 per cent. during the formation of the salt. F. Ephraim and P. Mosimann prepared **mercuric cobaltic aquopentamminobromide**,  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Br}_3 \cdot \text{HgBr}_2$ , in pale red, acicular crystals, which F. Ephraim and O. Schütz found to have the sp. gr. 3.279 at 25°, and the mol. vol. 232.5, corresponding with a vol. contraction of 53.7 per cent. in the formation of the compound. F. Ephraim and P. Mosimann also prepared **mercuric cobaltic aquopentamminobromide**,  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Br}_3 \cdot 3\text{HgBr}_2$ ; and F. Ephraim and O. Schütz found the sp. gr. to be 4.144 at 25°, and the mol. vol., 357.8, corresponding with a vol. contraction of 44.0 per cent. in the formation of the compound. E. Birk also studied the vol. relations of these salts. F. Ephraim and P. Mosimann were unable to prepare **lead cobaltic aquopentamminobromide**. H. Seibt, and A. Werner prepared the *cis*- and *trans*-forms of **cobaltic aquobisethylenediamineamminobromide**,  $[\text{Co}(\text{NH}_3)_2\text{en}_2(\text{H}_2\text{O})]\text{Br}_3 \cdot \text{H}_2\text{O}$ , by the action of potassium hydroxide or of freshly-precipitated silver oxide on the stereoisomeric cobaltic chloro- and bromo-bisethylenediamineammino salts. In every case, partial transformation takes place, so that a mixture of the isomerides is produced. The product of action of the alkali is an hydroxoammine salt, the aquoammine salt being produced when the soln. is acidified. Potassium hydroxide produces a greater relative transformation than silver oxide; more of the *trans*-isomeride is produced at low than at ordinary temp. The mixture of the isomerides is separated by taking advantage of the fact that the *trans*-salt is much less soluble in dil. hydrobromic acid than the *cis*-salt. The isomerides can be distinguished from each other (i) by transformation into the chloroamminodithionate by warming with hydrochloric acid, and subsequent precipitation with sodium dithionate; (ii) by warming the aq. soln., to which sodium nitrite and a little acetic acid has been added, to 60° to 70°. A yellow soln. is produced, which, on the addition of sodium dithionate, gives an insoluble precipitate if the *cis*-isomeride is present, or a precipitate which can be re-crystallized from water if the *trans*-isomeride is present. The *trans*-form gives brick-red acicular crystals, and the *cis*-form gives aggregates of small, red crystals. A. Gordienko studied the absorption spectrum. M. Rosner prepared **cobaltic aquobispyridinetriamminobromide**,  $[\text{Co}(\text{NH}_3)_3\text{py}_2(\text{H}_2\text{O})]\text{Br}_3$ .

S. M. Jörgensen<sup>5</sup> prepared **cobaltic diaquotetramminobromide**,  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{Br}_3$ , by adding 1:1-hydrobromic acid to a soln. of carbonatotetramminobromide, in 10 times its weight of cold water, until the evolution of carbon dioxide had ceased, and then adding conc. hydrobromic acid to the well-cooled liquid. The separation of dark red, octahedral crystals is almost quantitative. At 100°, the salt loses, in 30 mins., 1 mol. of water, and passes into the greyish-

violet aquobromotetramminobromide, and A. Werner, and F. Ephraim observed that the same transformation occurs when the solid is kept for some time, or if it be allowed to stand in contact with its soln. in 25 per cent. hydrobromic acid. A. Werner and A. Miolati found that the mol. conductivity,  $\mu$ , of a soln. of a mol of the salt in  $v$  litres, at 25°, to be :

$v$	.	.	.	125	250	500	1000	2000
$\mu$	.	.	.	325.5	354.8	379.8	399.5	417.4

The subject was studied by Y. Shibata. F. Ephraim found that a sat., aq. soln. at 22°, has 1.67 mols of the salt per litre. S. M. Jörgensen noted that with potassium ferricyanide, or cobalticyanide, the corresponding salts are precipitated from the aq. soln. Likewise with hydrochloroplatinic acid; and with hydrochloroauric acid and dil. sulphuric acid, a sulphatobromoaurate is precipitated.

E. Schmidt, and A. Werner and co-workers prepared **cobaltic cis-diaquobisethylenediaminebromide**,  $[\text{Co en}_2(\text{H}_2\text{O})_2]\text{Br}_3 \cdot 2\text{H}_2\text{O}$ , analogous with the bromide, starting from the carbonatobisethylenediaminebromide. J. C. Duff and E. J. Bills also prepared the salt in a similar manner. K. R. Lange, and A. Werner and co-workers observed that the red crystals pass, on keeping, into the violet *cis*-dibromo-bisethylenediaminebromide, and in the presence of acids, into the green *trans*-dibromo-salt. Four mols. of water are lost at 115°, and the green dibromo-salt is formed. The compound forms a yellowish-red, aq. soln. with an acidic reaction. Pyridine or potash-lye converts it into the *cis*-aquobromide. A. Werner and co-workers also prepared **cobaltic diaquobisethylenediaminebromide**,  $[\text{Co en}_2(\text{H}_2\text{O})_2]\text{Br}_3 \cdot 2\text{H}_2\text{O}$ , by the action of conc. hydrobromic acid on dinitratobisethylenediamine-thiocyanate, or on the hydroxyaquobisethylenediaminebromide. The pale violet-brown crystals form with water a dark reddish-brown soln., with an acidic reaction. On keeping, the salt goes into the violet *cis*-dibromobromide, and if an acid is present, green *trans*-dibromobromide is formed. The salt is dihydrated at 115°, forming the green *trans*-dibromobromide with a little of the *cis*-salt. A. Werner also prepared **cobaltic diaquobispyridinediamminobromide**,  $[\text{Co}(\text{NH}_3)_2\text{py}_2(\text{H}_2\text{O})_2]\text{Br}_3 \cdot 2\text{H}_2\text{O}$ , by the action of hydrobromic acid on the hydroxyaquobispyridinediamminochloride. The yellowish-brown, tabular crystals form, with a large proportion of water, a brownish-red soln. with an acidic reaction, and with a small proportion of water, or alcohol, hydroxyaquobispyridinediamminobromide.

#### *The CoA<sub>5</sub> or Pentammine Family.*

S. M. Jörgensen<sup>6</sup> prepared **cobaltic bromopentamminobromide**,  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Br}_2$ , by oxidizing an ammoniacal soln. of cobaltous bromide with air, and heating the soln. on a water-bath; or else by the action of hydrobromic acid on aquopentamminohydroxide, sulphate, or oxalate. The dichroic, bluish-violet, octahedral crystals are almost black, and the sp. gr. is 2.483 at 18°/4°. F. Ephraim gave 2.486 for the sp. gr. at 25°, and 154.4 for the mol. vol.; R. Klement, sp. gr. 2.512 at 25°/4°, and mol. vol., 152.9; and R. Lorenz and I. Posen, and I. Posen, in vacuo, 2.4739, and mol. vol. at absolute zero, 150.5. The vol. contraction in the formation of the salt was also studied by E. Birk, and W. Biltz. E. N. Gapon studied the diffusion. A. B. Lamb and J. P. Simmons gave -12.663 Cals. for the mol. heat of soln. at 25°. A. N. Nikolopulos, R. Luther and A. N. Nikolopulos, and J. Angerstein studied the absorption spectrum. A. Werner and A. Miolati found the mol. conductivity,  $\mu$ , for soln. with a mol of the salt in  $v$  litres, at 25°, to be :

$v$	.	.	.	.	250	500	1000	2000
$\mu$	.	.	.	.	230.5	244.7	257.6	268.1

Observations were also made by Y. Shibata. A. B. Lamb and J. W. Marden found that for soln. with 0.003266 mol per litre, at 25°, the value of  $\mu$  rose from 260.1 after 34 mins., to 287.2 after 1310 mins., to 353.1 after 2710 mins.; and, in the steady state, 402.0. The velocity constant for the transformation of the salt into aquopentamminobromide in these soln. was calculated by A. B. Lamb and J. W. Marden for a unimolecular reaction so that  $k=0.000170$ . J. N. Brønsted and R. Livingston said that the speed of aequation is almost independent of the initial concentration of the complex ions, but is dependent on the H<sup>+</sup>-ion concentration. A. B. Lamb and J. W. Marden observed that the reaction is almost com-

plete at 70°, for a 0.01302*M*-soln. in 0.02*M*-HBr, after 24 hrs., contained 98.10 per cent. of aquopentamminobromide. A. B. Lamb and J. P. Simmons found the mol. heat of this transformation is 1.69 Cals. at 25°. E. N. Gapon studied the ionic mobility; and N. R. Dhar and G. Urbain, the polarization tension—*vide supra*, the hexamminochloride. S. M. Jörgensen said that at 16°, 1 part of the salt requires 530 parts of water for its dissolution; F. Ephraim gave for a sat. soln. at 20°, 0.00614 mol per litre; and J. N. Brönsted and A. Petersen, 0.00275 mol per litre at 0°. The effect of salts on the solubility of bromopentamminobromide in water, and in methanol, was studied by J. N. Brönsted and co-workers. F. Ephraim said that the salt is virtually insoluble in hydrobromic acid, or in aq. soln. of ammonium or potassium bromide, as well as in alcohol. H. Freundlich and R. Bartels studied the hydrolysis of the salt. S. M. Jörgensen observed that a cold, freshly-prepared aq. soln. forms the corresponding salt of the series when it is treated with dil. nitric acid, dil. hydrochloric acid, potassium iodide, chromic acid, hydrochloroplatinic acid, or sodium bromoplatinate; silver chloride converts it into the chloride of the series; and silver oxide, carbonate, or nitrate produce the hydroxide and salts of aquopentammine, respectively. F. G. Soper studied the speed of the reaction with a mercuric salt.

S. M. Jörgensen prepared lilac needles of **mercuric cobaltic bromopentamminooctobromide**,  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Br}_2 \cdot 3\text{HgBr}_2$ ; and violet needles of **mercuric cobaltic bromopentamminobromoheptachloride**, by allowing a warm soln. of the bromopentamminobromide to run into an excess of a soln. of mercuric chloride; and if the bromopentamminobromide soln. be run into an excess of a soln. of sodium mercuric chloride,  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Cl}_2 \cdot \text{Br} \cdot 6\text{HgCl}_2$ , is formed in violet needles, and there is evidence of the formation of solid soln.

S. M. Jörgensen obtained **cobaltic bromopentamminodichloride**,  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Cl}_2$ , by treating a cold, aq. soln. of the bromide with dil. hydrochloric acid, or by pouring a soln. of the bromide in water at 40° into conc. hydrochloric acid. The dark, octahedral crystals are dichroic—violet to yellowish-red; the sp. gr. is 2.095 at 17°/4°; F. Ephraim and O. Schütz gave 2.087 at 25°, and the mol. vol. 141.3; R. Klement, 2.089 for the sp. gr. at 25°, and 141.3 for the mol. vol. E. Birk, and W. Biltz studied the vol. contraction in the formation of the compound. S. M. Jörgensen observed that the salt is sparingly soluble in cold water, but is more soluble than the bromide. F. Ephraim found that a sat. soln. at 20° has 0.0106 mol per litre; and J. N. Brönsted and co-workers found, at 0°, 0.00542 mol per litre, and at 20°, 0.011 mol; they also measured the solubility in the presence of other salts in aq. and in methanol soln. The heat of the transformation:  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Cl}_2 + [\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Br}_2 = [\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2 + [\text{Co}(\text{NH}_3)_5\text{Br}]\text{Br}_2$ , is 621 cals. at 0°. S. M. Jörgensen said that the salt is insoluble in dil. hydrochloric acid, and in alcohol. The cold, sat. soln. gives crystalline precipitates with dil. hydrobromic acid, hydrofluosilicic acid, sodium dithionate, ammonium oxalate, potassium dichromate, and potassium mercuric iodide. It forms violet needles of **mercuric cobaltic bromopentamminooctochloride**,  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Cl}_2 \cdot 3\text{HgCl}_2$ , when the nitrate of the series is treated with sodium mercuric chloride. E. Berl prepared **cobaltic bromobisethylenediaminehydroxylamine chloride**,  $[\text{Co}(\text{NH}_2\text{OH})_2\text{Br}]\text{Cl}_2$ .

H. Seibt prepared **cobaltic fluobisethylenediamineamminobromide**,  $[\text{Co}(\text{NH}_3)_2\text{F}]\text{Br}_2$ . S. M. Jörgensen prepared **cobaltic chloropentamminodibromide**,  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Br}_2$ , by treating the corresponding sulphate or nitrate with sodium bromide; by treating an aq. soln. of the carbonate with conc. hydrobromic acid; or by dissolving the chloride in dil. sulphuric acid at 50°, and pouring the cold soln. into well-cooled hydrobromic acid. H. Pitzler studied the equilibrium condition in the system:  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2 + 2\text{HBr} \rightleftharpoons [\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Br}_2 + 2\text{HCl}$ . According to S. M. Jörgensen, the reddish-violet crystals have a sp. gr. 2.15 at 25°, and a mol. vol. of 157.3; R. Klement gave 2.244 for the sp. gr. at 25°/4°, and 151.2 for the mol. vol. The vol. contraction in the formation of the compound was also studied by E. Birk, and W. Biltz. The absorption spectrum was studied by A. N. Nikolopulos, R. Luther and A. N. Nikolopulos, and J. Angerstein. A. Werner



and A. Miolati found the mol. conductivity,  $\mu$ , of soln. of a mol of the salt in  $v$  litres of water, at 25°, to be :

$v$	128	256	512	1025	2048
$\mu$	232.5	247.7	259.3	270.0	275.6

F. Ephraim found that a sat., aq. soln. at 19° contained 0.0178 mol per litre, and J. N. Brønsted and A. Petersen, at 0°, 0.00725 mol per litre. J. N. Brønsted studied the effect of other salts on the solubility in water, and in methanol. F. Ephraim observed on the solubility in water, and in methanol. F. Ephraim observed that no ammonia is taken up by the salt at -21°. S. M. Jørgensen prepared the complex:  $4[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Br}_2 \cdot 9\text{HgBr}_2$ . There is here evidence of the formation of solid soln.

E. Schmidt, and A. Werner prepared optically inactive or racemic **cobaltic-cis-bromobisethylenediamineamminobromide**,  $[\text{Co}(\text{NH}_3)_2\text{en}_2\text{Br}]\text{Br}_2 \cdot 2\text{H}_2\text{O}$ , by evaporating cis-nitrato-bisethylenediamineamminothiosulphate, with conc. hydrobromic acid; and A. Werner and W. E. Boës, and A. Werner and E. Scholze, by warming trans-dibromobisethylenediaminebromide with 1 : 1 aq. ammonia; or by warming diaquo-tetrol-quaterethylenediaminesulphate with a soln. of ammonium bromide, and then salting out the compound with sodium bromide. The *dihydrate* forms dark reddish-violet, rhombic crystals, and the anhydrous salt, dark brownish-red, prismatic crystals. The absorption spectrum was studied by A. Gordienko, Y. Shibata, and Y. Shibata and G. Urbain; and the magnetic properties, by L. C. Jackson, and W. Biltz. E. Rosenböhme gave  $-2.64 \times 10^{-7}$  mass unit for the magnetic susceptibility. A. Werner and E. Scholze obtained the *dextro-salt*, and the *levo-salt* from the corresponding camphor bromosulphonates. The sp. rotation of a 1 per cent. soln. of the *d-salt* is  $[\alpha] = 46.25^\circ$ , and for the *l-salt*,  $-45^\circ$ . A. Werner, and A. Werner and Y. Shibata found that liquid ammonia converts the active bromide into the corresponding active cis-bisethylenediaminediamminobromide, accompanied by a little of the trans-salt. E. Rosenböhme gave  $-3.44 \times 10^{-7}$  mass unit for the magnetic susceptibility. A. Werner, and A. Werner and W. E. Boës also prepared dark violet, prismatic crystals of **cobaltic trans-bromobisethylenediamineamminobromide**,  $[\text{Co}(\text{NH}_3)_2\text{en}_2\text{Br}]\text{Br}_2 \cdot 2\text{H}_2\text{O}$ , by the action of hydrobromic acid on the corresponding dithionate, or on an aq. soln. of trans-aquobisethylenediamineamminobromide; or by treating trans-thiocyanatobisethylenediamineamminobromide, first with conc. nitric acid, and then with hydrobromic acid. C. S. Borzekowsky prepared the *dextro-* and *levo-*forms of **cobaltic bromohydroxylaminebisethylenediaminebromide**,  $[\text{Co}(\text{NH}_2\text{OH})\text{en}_2\text{Br}]\text{Br}_2$ , as well as **cobaltic bromohydroxylaminebisethylenediaminechloride**,  $[\text{Co}(\text{NH}_2\text{OH})\text{en}_2\text{Br}]\text{Cl}_2$ .

H. Seibt prepared **cobaltic cis-fluobisethylenediamineamminobromide**,  $[\text{Co}(\text{NH}_3)_2\text{en}_2\text{F}]\text{Br}_2$ , by adding sodium bromide to a conc., aq. soln. of the corresponding fluoride. A. Gordienko, and J. Lifschitz and E. Rosenböhme studied the absorption spectrum. H. Seibt also prepared **cobaltic trans-fluobisethylenediamineamminobromide**, by treating the corresponding fluoride with ammonium fluoride. E. Berl obtained **cobaltic chlorobisethylenediaminehydroxylaminebromide**,  $[\text{Co}(\text{NH}_2\text{OH})\text{en}_2\text{Cl}]\text{Br}_2$ , and a double salt with platinous chloride.

A. Werner prepared bluish-red, optically-active or racemic **cobaltic cis-chlorobisethylenediamineamminobromide**,  $[\text{Co}(\text{NH}_3)_2\text{en}_2\text{Cl}]\text{Br}_2$ , by treating with conc. hydrobromic acid a soln. of *cis*-chloro-aquobisethylenediaminesulphate in conc. aq. ammonia—some *trans*-bisethylenediaminediamminobromide is formed at the same time. The salt is also prepared by salting out with sodium bromide a soln. of *trans*-dichlorobisethylenediaminechloride in liquid ammonia. The absorption spectrum was studied by J. Angerstein, and A. Gordienko. A. Werner and V. L. King treated the optically-active camphor bromosulphonates with sodium dithionate, and then acted on the product with hydrobromic acid. They thus obtained the *dextro-salt*, and the *levo-salt* in cherry-red, tabular crystals. The sp. rotation of 1 per cent. soln. had, with the C-line, the  $[\alpha] = 43.1^\circ$  for the *d-salt*, and  $-43.0^\circ$  for the *l-salt*. The salt is stable in aq. soln. and shows no sign of racemization at 70°. L. A. Welö gave  $-0.292 \times 10^{-6}$  for the magnetic susceptibility of the *d-salt*, and  $-0.035 \times 10^{-6}$  for the *l-salt*.

J. Meisenheimer and E. Kiderlen prepared violet plates of **cobaltic trans-chloroallylaminebisethylenediaminebromide**,  $[\text{Co en}_2(\text{C}_3\text{H}_5\text{NH}_2)\text{Cl}]\text{Br}_2$ , by the action of potassium bromide on the chloride. This salt is less soluble in water than the corresponding chloride; they also prepared reddish-violet, six-sided prisms of **cobaltic chloroallylaminebisethylenediaminebromide**,  $[\text{Co en}_2(\text{C}_3\text{H}_5\text{NH}_2)\text{Cl}]\text{Br}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ , in a similar manner; likewise reddish-violet, six-sided prisms of **cobaltic chloroanilinebisethylenediaminebromide**,  $[\text{Co en}_2(\text{C}_6\text{H}_5\text{NH}_2)\text{Cl}]\text{Br}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ ; also brownish-red, and violet-red plates of **cobaltic chloro-*p*-toluidinebisethylenediaminebromide**,  $[\text{Co en}_2(\text{C}_7\text{H}_7\text{NH}_2)\text{Cl}]\text{Br}_2$ ; and lilac **cobaltic chlorobenzylaminebisethylenediaminebromide**,  $[\text{Co en}_2(\text{C}_7\text{H}_7\text{NH}_2)\text{Cl}]\text{Br}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ . R. Vogel prepared **cobaltic chloropyridinebisethylenediaminebromide**,  $[\text{Co en}_2\text{pyCl}]\text{Br}_2$ .

A. Werner obtained **cobaltic hydroxypentamminobromide**,  $[\text{Co}(\text{NH}_3)_5(\text{OH})]\text{Br}_2$ .

H<sub>2</sub>O, by heating aquopentamminobromide with conc. hydrobromic acid, and precipitating the salt with alcohol. The bluish-red salt is readily soluble in water, and the bluish-red soln. has an alkaline reaction. The absorption spectrum was studied by J. Angerstein. A. Werner, and K. R. Lange also obtained **cobaltic hydroxyaquotetramminobromide**,  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{OH})]\text{Br}_2$ , in carmine-red crystals, by saturating a soln. of the chloride with potassium bromide. H. J. S. King found the eq. conductivity, at 0°, to be :

$\nu$	.	.	64	128	256	512	1024	$\infty$
$\lambda$	.	.	116.3	123.7	129.6	134.7	137.0	146.9

A. Oswald studied the physiological action.

M. Rosner prepared **cobaltic hydroxybispyridinetriamminobromide**,  $[\text{Co}(\text{NH}_3)_3\text{py}_2(\text{OH})]\text{Br}_2 \cdot 2\text{H}_2\text{O}$ . A. Werner, and A. Werner and S. Matissen prepared **cobaltic cis-hydroxy-aquobisethylenediaminebromide**,  $[\text{Co en}_2(\text{H}_2\text{O})(\text{OH})]\text{Br}_2 \cdot \text{H}_2\text{O}$ , by warming cis-hydroxy-bromobisethylenediaminebromide with a little water; by the action of pyridine in aq. soln. on diaquobisethylenediaminebromide, by the action of dil. potash-lye on green or violet trans-dichlorobisethylenediaminechloride, followed by treatment with conc. hydrobromic acid; or by the action of potash-lye on a soln. of carbonatobisethylenediaminebromide in dil. nitric acid and subsequent treatment with sodium bromide. The bluish-red crystalline powder decomposes at 115°. It is less soluble in water than the corresponding chloride. Potassium bromide and iodide precipitate the corresponding salts from the aq. soln.; silver nitrate precipitates silver bromide free from silver oxide; and conc. hydrochloric or hydrobromic acid forms cis-diaquobisethylenediaminebromide; carbon dioxide acts on the aq. soln. forming a carbonatobromide. The boiling aq. soln. decomposes, forming trisethylenediaminebromide, and hexol-sexiesethylenediaminebromide. The magnetic properties were studied by L. C. Jackson; and E. Rosenbohm gave  $-3.09 \times 10^{-7}$  mass unit for the magnetic susceptibility. A. Werner also prepared **cobaltic trans-hydroxyaquobisethylenediaminebromide**, by warming trans-diaquobisethylenediaminebromide with conc. aq. ammonia; by boiling the cis-salt with 1:1-potash-lye, and then neutralizing the ice-cold liquor with hydrobromic acid; by triturating a soln. of cis-dichlorobisethylenediaminechloride with solid sodium bromide; and by warming trans-dibromobisethylenediaminebromide with dil. aq. ammonia until red crystals began to form. The pale bluish-red crystals are less soluble in water than the corresponding chloride. The mol. wt. by the f.p. method is 139. L. C. Jackson studied the magnetic properties, and E. Rosenbohm gave  $-3.09 \times 10^{-7}$  mass unit for the magnetic susceptibility. A. Werner found that carbon dioxide, led into the ice-cold soln., forms carbonatobisethylenediaminebromide.

A. Werner reported **cobaltic hydroxyaquobispyridinediamminobromide**,  $[\text{Co}(\text{NH}_3)_2\text{py}_2(\text{H}_2\text{O})(\text{OH})]\text{Br}_2$ , by the addition of potassium bromide to an acetic acid soln. of the corresponding chloride; by mixing a sat. soln. of diaquobispyridinediamminochloride with potassium bromide, or by treating the corresponding bromide with water, or by adding hydrobromic acid to the aq. soln. The small, violet crystals are sparingly soluble in water, and the soln. reacts feebly alkaline.

A. Werner<sup>7</sup> prepared **cobaltic cis-chloroaquotetramminobromide**,  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2\text{Cl}]\text{Br}_2$ , by simply keeping cis-diaquotetramminobromide for a long time; and S. M. Jörgensen, by adding a sat., aq. soln. of the corresponding chloride to ice-cold, conc. hydrobromic acid. The bluish-violet crystals are more soluble in water than is the corresponding chloride, and almost insoluble in 1:1-hydrobromic acid.

A. Werner, and A. Werner and G. Tschernoff obtained **cobaltic chloroaquobisethylenediaminebromide**,  $[\text{Co en}_2(\text{H}_2\text{O})\text{Cl}]\text{Br}_2 \cdot \text{H}_2\text{O}$ , by triturating the corresponding sulphate with conc. hydrobromic acid, and precipitating the salt with hydrobromic acid from ice-cold soln. A. Gordienko measured the absorption spectrum. A. Uspensky and K. Tschibisoff noticed that when the soln. of the salt in conc. hydrobromic acid is evaporated, a complex mixture containing cis- and trans-bromochlorobisethylenediaminebromide, and trans-dibromobisethylenediaminebromide is formed. H. Fischlin, and A. Werner and J. E. Schwyzer prepared the *dextro*-salt, and the *levo*-salt from the corresponding camphor-bromosulphonates. The sp. rotation of a 1 per cent. soln. of the *d*-salt is  $[\alpha] = 215^\circ$ , and of the *l*-salt,  $-215^\circ$ . H. Fischlin, and J. Lifschitz studied the rotary dispersion. Conc. aq. ammonia transforms these salts into active chlorohydroxy-salts; and with acetylacetone or propionylacetone, A. Werner and J. E. Schwyzer observed that optically active acetylacetonatobisethylenediamine or propionylacetonatobisethylenediamine-salts are formed.

A. Werner prepared **cobaltic chlorodiaquotriaminobromide**,  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_2\text{Cl}]\text{Br}_2$ , by pouring an ice-cold soln. of the corresponding chloride into cold, conc. hydrobromic acid, and draining the precipitate on porous tiles. The small, dark blue needles can be preserved over potassium hydroxide, but the salt is very unstable. In air, it forms bromochloro-aquotriaminobromide. It forms a blue soln. in water, and from the ice-cold soln., hydrobromic acid precipitates the monohydrate of bromochloro-aquotriaminobromide.

A. Werner, and A. Werner and A. Wolberg prepared **cobaltic bromoaquatetramminobromide**,  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Br}]\text{Br}_2$ , by keeping *cis*-diaquotetramminobromide for some time; or by adding alcohol to an aq. soln. of dibromotetramminobromide acidulated with hydrobromic acid, at  $40^\circ$ ; W. Schramm, by the action of malonic acid on *trans*-dibromotetramminobromide; and A. Werner and A. Miolati, by treating bromocarbonatotetramminobromide with hydrobromic acid. The brownish-violet prisms form a violet, aq. soln. which soon changes to a rose-colour owing to aquation. A. Werner and A. Miolati found that the mol. conductivity,  $\mu$ , for a mol of the salt in  $v$  litres of water, at  $25^\circ$ , is:

$v$	.	.	.	125	250	500	1000	2000
$\mu$	.	.	.	320.4	349.4	377.3	395.4	413.6

and they added that the results agree with those obtained with diaquotetramminobromide. A. Werner and A. Wolberg observed that ammonium thiocyanate converts the salt into what is probably a thiocyanatotetrammine; and W. Schramm, that oxalic acid forms oxalatotetrammine, and malonic acid forms a trace of dibromotetramminobromide. A. Werner and A. Wolberg found that by digesting this salt with conc. hydrochloric acid of sp. gr. 1.17, small, violet prisms of **cobaltic bromoaquatetramminochloride**,  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Br}]\text{Cl}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ , are formed. J. Angerstein studied the absorption spectrum.

E. Schmidt, and A. Werner and R. Schmidt prepared **cobaltic bromoaquobisethylenediaminebromide**,  $[\text{Co en}_2(\text{H}_2\text{O})\text{Br}]\text{Br}_2 \cdot \text{H}_2\text{O}$ , by the following methods: (1) A soln. of neutral *trans*-dichlorobisethylenediaminechloride containing nitric acid is heated with a conc. soln. of silver nitrate until it assumes a Bordeaux-red colour. After collecting the silver bromide, the filtrate is saturated with sodium bromide, first filtering off any more silver bromide which may be formed. After a few hours, the bromide has deposited as a violet, microcrystalline powder. (2) A conc. soln. of the *trans*-dibromo-bromide is heated at  $40^\circ$  until it becomes violet in colour; after cooling, it is saturated with sodium bromide. Any green crystals of dichloro-bromide which are precipitated with the bromoaquo-bromide are removed by fractional soln. in ice-cold water, the dichloro-bromide being the less-soluble salt. (3) A soln. of the *trans*-dibromonitrate is treated similarly to the dibromobromide, except that it is heated over the bare flame. (4) The carbonato-chloride or bromide is treated with conc. hydrobromic acid ( $d=1.4$ ). The bromoaquo-bromide is separated from the less soluble *cis*-dibromo-bromide, which is formed at the same time, by fractional soln. (5) *Cis*-diaquo-bromide is heated at  $40^\circ$  with just enough water to give complete soln. until a violet-coloured soln. is obtained; the bromoaquo-salt is then precipitated with sodium bromide. The dark violet, tabular crystals are readily soluble in water, forming a reddish-violet liquid. A. Gordienko studied the absorption spectrum. A. Werner and R. Schmidt, and A. Uspensky and K. Tschibisoff observed that conc. hydrobromic acid converts the salt into *cis*-dibromobisethylenediamine bromide and a little of the *trans*-salt; whilst conc. hydrochloric acid forms a complex mixture containing *cis*- and *trans*-bromochlorobisethylenediaminechloride, and chlorobisethylenediaminechloride. W. Tupizina prepared **cobaltic bromopyridinebisethylenediaminebromide**,  $[\text{Co en}_2\text{prBr}]\text{Br}_2$ .

#### *The CoA<sub>4</sub> or Tetrammine Family.*

A. Werner and A. Miolati<sup>8</sup> prepared **cobaltic dibromotetramminobromide**,  $[\text{Co}(\text{NH}_3)_4\text{Br}_2]\text{Br}$ , by treating the diaquotetramminobromide with conc. hydrobromic acid; and A. Werner and A. Wolberg, by treating carbonatotetramminobromide with conc. hydrobromic acid, or by the action of hydrobromic acid on a soln. of the corresponding chloride. H. and W. Biltz thus describe the preparation of this salt:

Shake, in a flask, 20 grms. of cobaltic carbonatotetramminonitrate with 80 grms. of conc. hydrochloric acid, and continue shaking while the flask is being slowly heated over

a free flame. Much carbon dioxide is evolved, and the colour changes from a reddish-brown to a pale brown, and, finally, to a dull green. When the colour-change has ceased, let the mixture cool to the temp. of the room, and add 50 c.c. of cold water so as to dissolve a little admixed bromoaquo-bromide. Drain the precipitate on a hardened filter, and wash it with cold water until the filtrate is no longer greyish-brown, but colourless. The yield is 24 grms. of a fine, light yellowish-green, sparingly-soluble powder.

G. and P. Spacu prepared **bismuth cobaltic dichlorobisethylenediaminebromide**,  $[\text{Co en}_2\text{Cl}_2]\text{BiBr}_6$ ; and **stannic cobaltic dichlorobisethylenediaminebromide**,  $[\text{Co en}_2\text{Cl}_2]\text{SnBr}_6$ .

F. de Boër studied the X-ray absorption spectrum of aq. soln. A. Werner and A. Miolati observed that the dibromotetrammine in aq. soln. rapidly passes into the diaquotetrammine, so that with a soln. of a mol in 500 litres, at 25°, the conductivity rises in 40 mins. from  $\mu=190.5$  to 363.5. The final value corresponds with that obtained with the diaquo-bromide. According to A. Werner, and A. Werner and A. Wolberg, when the salt is heated with a little water, it forms hexol-dodecamminobromide; and, according to W. Schramm, oxalic acid forms some oxalatotetramminobromide, but the analogous substitution does not occur with malonic acid. A. Werner and A. Wolberg observed that when the dibromoamminobromide is triturated with cold, conc. hydrochloric acid, and, after 8 hrs., washed with ice-cold water, and the soln. poured into conc. hydrochloric acid, dark violet, prismatic needles of **cobaltic dibromoamminochloride**,  $[\text{Co}(\text{NH}_3)_4\text{Br}_2]\text{Cl}$ , are formed. The salt decomposes at 100°. The green aq. soln. soon changes into a violet soln. of the diaquotetrammine. This salt forms, with auric chloride, pale green, soluble, acicular crystals of **gold cobaltic dibromotetramminotetrachloride**,  $[\text{Co}(\text{NH}_3)_4\text{Br}_2]\text{AuCl}_4$ .

A. Werner, E. Schmidt, and W. Tupizina observed that cobaltic *violobromide*, or **cobaltic cis-dibromobisethylenediaminebromide**,  $[\text{Co en}_2\text{Br}_2]\text{Br}$ , is formed when *cis*- or *trans*-diaquobisethylenediaminebromide is kept for some time; and when bromoaquobisethylenediaminebromide or a sulphitobisethylenediamine salt is treated with hydrobromic acid; and A. Werner and co-workers also found that the *cis*-salt can be obtained by the following processes: (1) A solution of the *trans*-bromide is evaporated on the water-bath several times to a syrupy consistency. On keeping in a vacuum desiccator, black crystals are then obtained, which give a greyish-violet powder; they consist chiefly of the *cis*-isomeride mixed with a little of the *trans*-isomeride. The latter can be extracted with a small quantity of water, leaving the *cis*-form, which can be purified by soln. in water and precipitation with sodium bromide. (2) By fission of diol-quaterethylenediaminebromide with conc. hydrobromic acid into diaquo-bromide and the required dibromo-bromide. The diaquo-salt is removed from the mixture by soln. in absolute alcohol. (3) From carbonatobisethylenediaminebromide by treatment with an alcoholic or aq. soln. of hydrogen bromide by a method similar to that described for the corresponding dichloro-salts. The salt can be purified by precipitation with sodium bromide from its aq. soln. The *cis*-bromide furnishes scaly crystals with a colour and lustre resembling those of graphite. A. Gordienko, and M. L. Ernsberger and W. R. Brode studied the absorption spectrum. K. Matsuno observed that the aequation in aq. soln. can be represented by the equations:  $[\text{Co en}_2\text{Br}_2]\text{Br} \rightarrow [\text{Co en}_2(\text{H}_2\text{O})\text{Br}]\text{Br}_2 \rightarrow [\text{Co en}_2(\text{H}_2\text{O})_2]\text{Br}_3$ . A. Werner found that conc. hydrobromic acid converts the violet *cis*-salt into the green *trans*-salt; and liquid ammonia produces a mixture of *cis*- and *trans*-bisethylenediaminediamminobromide. S. M. Jörgensen prepared **cobaltic praseoehloride**, or **cobaltic trans-dibromobisethylenediaminebromide**. A. Werner observed that when *cis*- and *trans*-diaquobisethylenediaminebromides are kept for a long time, or when they are heated to 105°; by the action of warm hydrobromic acid on chloroaquobisethylenediaminebromide, or the chloro-bromide, or the sulphato-chloride; and W. Schramm, by the action of malonic acid on *cis*-diaquobisethylenediaminebromide—the yield is small. A. Werner and co-workers also gave these methods of preparation: (a) A soln. of cobalt bromide in 10 per cent. ethylenediamine is oxidized by leading air through it, and then evaporated to dryness. The residue is then repeatedly treated with hydrobromic acid and evaporated until a uniform green salt remains, which consists of the acid bromide. On treatment with a little water, the *trans*-bromide is obtained. (b) Carbonatobisethylenediaminebromide is heated on the water-bath with a soln. of hydrobromic acid, of sp. gr. = 1.49, until the soln. is green. On cooling, the acid bromide separates, from which the normal bromide is best obtained by heating at 110° until it no longer gives an acidic soln. The siskin-green crystals, found by S. M. Jörgensen, have a 4 per cent. solubility in water. A. Gordienko, C. Schleicher, and M. L. Ernsberger and W. R. Brode, studied the absorption spectrum. S. M. Jörgensen observed that the aq. soln. becomes dark red when boiled, owing to the formation of the aquo-salt;

A. Werner said that *cis*-bromoquo-bromide is formed; conc. aq. ammonia converts the salt into *cis*-bromobisethylenediamineamminobromide, and liquid ammonia produces *cis*-bisethylenediaminediamminobromide with a little of the trans-salt. According to S. M. Jørgensen, 1:1-hydrochloric acid gives no precipitate, but crystalline precipitates are produced in a 4 per cent. soln. by the addition of dil. nitric acid, sodium dithionate or bromoplatinate, and by potassium iodide, bromomercurate, or ferrioyanide—potassium ferrocyanide colours the soln. red. W. Schramm found that oxalic acid forms the oxalato-bromide, whilst malonic acid gives a mixture of violet bromoquo-bisethylenediaminebromide, and green dibromobisethylenediaminebromide. H. Seibt prepared **cobaltic difluorobisethylenediaminebromide**,  $[\text{Co en}_2\text{F}_2]\text{Br}$ . S. M. Jørgensen, and A. Werner obtained crystals of **cobaltic dibromobisethylenediaminebromide**,  $[\text{Co en}_2\text{Br}_2]\text{Br} \cdot 2\text{H}_2\text{O}$ ; according to H. Grossmann and B. Schück, the salt is a monohydrate, of m.p.  $214^\circ$ . The constitution was discussed by A. Werner, and T. S. Price and S. A. Brazier. S. M. Jørgensen, and T. S. Price and J. C. Duff noted the formation of **mercuric cobaltic dibromobisethylenediaminebromide**,  $[\text{Co en}_2\text{Br}_2]\text{Br} \cdot \text{HgBr}_2$ . A. Werner and A. Grün treated a conc. aq. soln. of cobaltic bromochloroquoethylenediamineamminobromide with its own vol. of hydrobromic acid, and obtained green, stellar aggregates of crystals of cobaltic **dibromoquoethylenediamineamminobromide**,  $[\text{Co}(\text{NH}_3)_2\text{en}(\text{H}_2\text{O})\text{Br}_2]\text{Br}$ , which are dichroic—bluish-black, and brown. G. Lindenberg prepared **cobaltic dibromobisethylenediaminebromide**,  $[\text{Co tr}_2\text{Br}_2]\text{Br}$ .

A. Werner and A. Grün reported **cobaltic dibromoquoethylenediamineamminobromide**,  $[\text{Co}(\text{NH}_3)_2\text{en}(\text{H}_2\text{O})\text{Br}_2]\text{Br}$ , by warming bromochloroquoethylenediamineamminobromide with water, and then an equal vol. of hydrobromic acid of sp. gr. 1.49. The small, stellate aggregates of needles are strongly dichroic from bluish-black to brown, and when powdered, the salt is green. It forms a brown soln. with water.

A. Werner prepared **cobaltic cis-dichlorotetramminobromide**,  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Br}$ , by the action of an aq. soln. of ammonium bromide on the corresponding dithionate, and precipitation from the aq. soln. by ammonium bromide. The violet-blue crystals are sparingly soluble in water, and the blue, aq. soln. rapidly changes to violet because of the formation of the aquo-salt. S. M. Jørgensen, and A. Werner and A. Klein also obtained **cobaltic trans-dichlorotetramminobromide** by adding hydrobromic acid to an aq. soln. of the sulphate. The green, rhombic crystals were found by F. Ephraim and O. Schütz to have a sp. gr. of 2.143 at  $25^\circ$ , a mol. vol. of 129.7, and a vol. contraction of 59.6 per cent. in the formation of the salt. When heated at  $100^\circ$  for 24 hrs., it loses 2 per cent., and in 6 weeks, 25 per cent. in weight. A. N. Nikolopulos, and R. Luther and A. N. Nikolopulos studied the absorption spectrum. A. Werner and A. Miolati found that the mol. conductivity of a soln. of a mol. of the salt in 512 litres of water at  $25^\circ$ , changes in 40 mins. from  $\mu = 116.6$  to 332.1, as the green soln. passes to a violet-red soln. of the aquo-salt. The aquation was studied by L. Tschugaeff. J. N. Brønsted and co-workers found that a sat. aq. soln. at  $0^\circ$  contains 0.00632 mol per litre, and they studied the effect produced by the presence of different salts. A. Werner said that silver nitrate precipitates from the soln. what is probably a double salt.

A. Werner and R. Feenstra reported **cobaltic trans-dichloroquaterpyridinobromide**,  $[\text{Co py}_4\text{Cl}_2]\text{Br}$ , to be formed by the action of potassium bromide on a soln. of the corresponding chloride. The pale blue crystals can be freed from water only by long-continued drying in the desiccator. P. Larisch prepared **cobaltic dichlorobisethylenediaminebromide**,  $[\text{Co en}_2\text{Cl}_2]\text{Br} \cdot \text{H}_2\text{O}$ , in violet crystals, by the action of solid potassium bromide on a cold, sat. soln. of the corresponding chloride; 100 c.c. of water at  $1^\circ$  dissolve 0.878 grm. of the salt. A. Werner, and A. Werner and G. Tschernoff obtained the *dextro*-salt and the *laevo*-salt, in indigo-blue crystals, by adding alcohol to a soln. of the camphor bromosulphonates in hydrobromic acid. The sp. rotation of a 0.25 per cent. soln. is  $[\alpha] = 168^\circ$  for the *dextro*-salt, and  $[\alpha] = -176^\circ$  for the *laevo*-salt. S. M. Jørgensen obtained **cobaltic trans-dichlorobisethylenediaminebromide**, as a matte green powder by treating the corresponding chloride with hydrobromic acid. E. Petersen measured the lowering of the f.p., and the mol. conductivity of the soln. at  $0^\circ$  and  $25^\circ$ , and inferred that at  $0^\circ$  the salt is stable in aq. soln. The subject was discussed by A. Werner and C. Herty, and W. D. Harkins and co-workers. G. and P. Spacu prepared the double salt: **cadmium cobaltic dichlorobisethylenediaminebromide**,  $[\text{Co en}_2\text{Cl}_2]_2\text{CdBr}_4$ . A. Werner and A. Fröhlich, and H. E. Watts prepared **cobaltic trans-dichlorobispropyldiaminebromide**,  $[\text{Co pn}_2\text{Cl}_2]\text{Br} \cdot \text{H}_2\text{O}$ , by the action of potassium bromide on the corresponding chloride. The matte green, crystalline powder is very soluble in water, but cannot be re-crystallized from aq. soln. A. Werner and F. Chaussy obtained **cobaltic cis-dichloroethylenediaminediamminobromide**,  $[\text{Co}(\text{NH}_3)_2\text{enCl}_2]\text{Br}$ , as a violet-blue precipitate, by treating carbonatoethylenediamine-diamminochloride with very conc. hydrochloric acid at  $-16^\circ$ , when the development of

carbon dioxide has ceased, adding ammonium bromide; **cobaltic trans-dichloroethylenediaminediamminobromide**, was likewise formed as a green precipitate, by the action of hydrobromic acid or ammonium bromide on a conc., aq. soln. of the chloride at 0°.

A. Werner prepared **cobaltic cis-hydroxychlorobisethylenediaminebromide**,  $[\text{Co en}_2(\text{OH})\text{Cl}]\text{Br}$ , in brownish-violet crystals, by adding conc. ammonia to chloroaquobisethylenediaminebromide. In warm aq. soln., aquation occurs, and the cis-hydroxyaquobromide is formed, and with hot, conc. hydrochloric acid, cis-dichloro-chloride, accompanied by a small proportion of trans-dichlorochloride, is formed. The *dextro-salt* and the *levo-salt*, as monohydrates, were prepared by H. Fischlin from the corresponding chloroaquobromides by treatment first with conc. ammonia, and then with 1 : 1-alcohol. After washing with a little conc., aq. ammonia, the brownish-violet crystals are dried by alcohol and ether. The sp. rotation of a 0.1 per cent. aq. soln. of the *dextro-salt* is  $[\alpha] = 695^\circ$ , and of the *levo-salt*,  $-687^\circ$ .

A. Werner reported **cobaltic hydroxybromobisethylenediaminebromide**,  $[\text{Co en}_2(\text{OH})\text{Br}]\text{Br}$ , to be formed as a brownish-violet salt by treating bromoaquobisethylenediaminebromide with conc. ammonia. When the salt is warmed with a little water, aquation occurs and the cis-hydroxyaquobromide is formed; and when triturated with conc. hydrobromic acid, the cis-diaquo-bromide is produced. A. Gordienko studied the absorption spectra of aq. soln. A. Werner also prepared, in a similar manner, **cobaltic hydroxychlorobisethylenediaminebromide**,  $[\text{Co en}_2(\text{OH})\text{Cl}]\text{Br}$ , as a brownish-violet mush of crystals, by treating chloroaquobisethylenediaminebromide with conc. ammonia. With hot, conc. hydrochloric acid, it forms cis-dichloro-chloride accompanied by a small proportion of trans-dichloro-chloride.

A. Werner and A. Grün prepared **cobaltic bromochloroaquotriamminobromide**,  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})\text{ClBr}]\text{Br}$ , by the action of fuming hydrobromic acid on the chloroaquotriamminosulphate. The olive-green crystals furnish a green soln. which quickly turns blue. If an aq. soln. of blue chlorodiaquotriamminobromide is treated with hydrobromic acid, or if conc. hydrobromic acid is added to an aq. soln. of dichloroaquotriamminochloride, chocolate-brown crystals of the *monohydrate* are formed. The soln. in water is green at 0°, bluish-violet at ordinary temp., and red at higher temp. The crystals lose a mol. of water at 100°. Potassium iodide precipitates the brown iodide from the cold, aq. soln., and conc. nitric acid, the green nitrate.

A. Werner, and A. Werner and G. Tschernoff prepared **cobaltic bromochlorobisethylenediaminebromide**,  $[\text{Co en}_2\text{ClBr}]\text{Br} \cdot \text{H}_2\text{O}$ , by covering 2 grms. of chlorobisethylenediaminebromide with 2 c.c. of conc. hydrobromic acid, and the mixture heated until complete soln. takes place. On cooling, a mixture of the green and violet salt is obtained, which is washed with alcohol and ether, dried, and then treated with a small quantity of water to dissolve out the green salt. The violet salt (cis-isomeride) is collected, washed with water and alcohol, and dried. The green filtrate gives precipitates with metallic salts, which give analytical results corresponding with a mixture of dibromo- and chlorobromo-salts. The salt is also formed when chloroaquobisethylenediaminebromide is heated for 2 hours at 110°, whereby a mixture of the cis- and trans-chlorobromo-bromides is produced. This is separated as before. The *dextro-salt*, and the *levo-salt* are derived from the corresponding camphor bromosulphonates, in dark greyish-violet, crystalline powders, which lose a mol. of water at 110°. The sp. rotation of the *dextro-salt* is  $[\alpha] = 148^\circ$ , and of the *levo-salt*,  $-155^\circ$ . M. L. Ernsberger and W. R. Brode studied the absorption spectrum. The corresponding **cobaltic bromochlorobisethylenediaminechloride**,  $[\text{Co en}_2\text{ClBr}]\text{Cl} \cdot \text{H}_2\text{O}$ , was prepared in an analogous manner as dark greyish-violet crystalline powder. The sp. rotation of the *dextro-salt* is  $[\alpha] = 164^\circ$ , and of the *levo-salt*,  $-176^\circ$ . If a conc. soln. of dichloroaquoethylenediamineamminochloride is treated with hydrobromic acid, **cobaltic bromochloroaquoethylenediamineamminobromide**,  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})\text{ClBr}]\text{Br}$ , is formed in olive-green crystals. Conc. nitric acid converts it into the nitrate, and potassium iodide, into the iodide of the series.

### *The $\text{CoA}_3$ or Triammine Family.*

E. Birk<sup>9</sup> prepared **cobaltic tribromotriammine**,  $[\text{Co}(\text{NH}_3)_3\text{Br}_3]$ , by treating triol-hexamminobromide with conc. hydrobromic acid.

### *Complexes with Two or More Cobalt Atoms.*

A. Werner<sup>10</sup> prepared **cobaltic  $\mu$ -amino-decamminobromide**,  $[(\text{NH}_3)_5\text{Co} - \text{NH}_2 \cdots \text{Co}(\text{NH}_3)_5]\text{Br}_5 \cdot \text{H}_2\text{O}$ , by the action of ammonium bromide on the nitrate, sulphate, or dithionate. The reddish-brown needles form a 0.5 per cent. soln.

with water at room temp. Ammonium bromide precipitates the salt almost quantitatively from its aq. soln. The salt loses water at 80° to 85° without decomposition, but with warm, conc. sulphuric or nitric acid, the hexammino- and chloropentammino-salts are formed.

A. Werner, and A. Baselli, prepared **cobaltic bromoaquo- $\mu$ -amino-octamminobromide**,  $[(\text{H}_2\text{O})(\text{NH}_3)_4\text{Co}-\text{NH}_2\cdots\text{Co}(\text{NH}_3)_4\text{Br}]\text{Br}_4$ , by the action of conc. hydrobromic acid on  $\mu$ -amino-ol-octamminosulphate. The dark brown, acicular crystals dissolve in water, and the reddish-brown soln. has an acidic reaction; the aq. soln. soon becomes carmine-red owing to the formation of  $\mu$ -amino-ol-octamminobromide.

A. Werner and F. M. Grigorieff, and I. Fürstenberg obtained **cobaltic tetrabromo- $\mu$ -amino-hexamminobromide**,  $[\text{Br}_2(\text{NH}_3)_3\text{Co}-\text{NH}_2\cdots\text{Co}(\text{NH}_3)_3\text{Br}_2]\text{Br}\cdot 2\text{H}_2\text{O}$ , by warming an aq. soln. of  $\mu$ -amino-diol-hexamminobromide with conc. hydrobromic acid on the water-bath. The salt is also prepared by reducing  $\mu$ -amino-peroxo-ol-hexamminobromide with sulphurous acid, and the addition of conc. hydrobromic acid to the resulting soln. gives greenish-black crystals. The greenish-brown, crystalline powder loses 2 mols. of water at 70° to 80°; it is insoluble in cold water; an acidified soln. of silver nitrate,  $\mu$ -amino-diol-hexamminonitrate or diaquo- $\mu$ -amino-ol-hexamminonitrate is formed in aq. soln.

A. Werner prepared **cobaltic diol-octamminobromide**,  $[(\text{NH}_3)_4\text{Co}\cdots(\text{OH})_2\cdots\text{Co}(\text{NH}_3)_4]\text{Br}_4\cdot 4\text{H}_2\text{O}$ , by treating the corresponding chlorides with a sat. soln. of potassium bromide. The ruby-red crystals are freely soluble in water, and potassium bromide precipitates the salt from its aq. soln. Two mols. of water are lost over sulphuric acid; and all is given off at 80°. Observations on the salt were made by H. Frank; L. C. Jackson studied the magnetic properties; and E. Rosenbohm gave  $-1.19 \times 10^{-7}$  mass unit for the magnetic susceptibility.

A. Werner and J. Rapport prepared **cobaltic diol-quaterethylenediaminebromide**,  $[\text{en}_2\text{Co}\cdots(\text{OH})_2\cdots\text{Co en}_2]\text{Br}_4\cdot 4\text{H}_2\text{O}$ . The action of conc. hydrochloric acid on hexol-sexiesethylenediaminenitrate, furnishes crystals of cis-diaquobis-ethylenediaminechloride, and, when this product is digested with pyridine and sodium dithionate, it yields crystals of cis-hydroxyaquobisethylenediaminedithionate. This salt at 100° to 110° loses water, to form the dithionate of the required salt. When the dithionate is triturated with ammonium bromide and water, it yields reddish-violet needles of the *tetrahydrate*, which loses two mols. of water at 100°, or over conc. sulphuric acid, forming the *dihydrate*. The preparation of the salt was also described by H. Frank, and by J. V. Dubskey. L. C. Jackson studied the magnetic properties; and E. Rosenbohm found the magnetic susceptibility to be  $-2.64 \times 10^{-7}$  mass unit. A. Werner and J. Rapport found that at 12°, fuming hydrobromic acid converts the salt into cis-dibromobis-ethylenediaminebromide.

A. Werner prepared **cobaltic  $\mu$ -diamino-octamminobromide**,  $[(\text{NH}_3)_4\text{Co}\cdots(\text{NH}_2)_2\cdots\text{Co}(\text{NH}_3)_4]\text{Br}_4\cdot 4\text{H}_2\text{O}$ . He said that in the preparation of cis-dichlorotetramminochloride from diol-octamminochloride, the crude substance sometimes assumes a superficial red colour when dried over phosphorus pentoxide. If this partly-changed product is dissolved in water, and sodium dithionate added after half an hour, orange-yellow crystals of  $\mu$ -diamino-octamminodithionate are precipitated, and on triturating the precipitate with a little water and ammonium bromide, red crystals of the *tetrahydrate* are formed.

A. Werner obtained **cobaltic hydroxyaquo-peroxo-ol-hexamminobromide**,  $[(\text{OH})(\text{NH}_3)_3\text{Co}=(\text{OH})\text{O}_2\cdots\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})]\text{Br}_3$ , by rubbing up the sulphate with ammonium bromide and a little water. The greenish-brown needles form, with water, a brown soln. having a feebly acidic reaction. The solid becomes red on keeping.

A. Werner,<sup>11</sup> prepared **cobaltic  $\mu$ -ammonium-peroxo-quaterethylenediaminebromide**,  $[\text{en}_2\text{Co}=\text{O}_2(\text{HN.HBr}_3)=\text{Co en}_2]\text{Br}_3\cdot 3\text{H}_2\text{O}$ , by treating a soln. of the corresponding nitrate with potassium bromide; red crystals of the *trihydrate* are formed. The crystals dissolve in water, which is turned red, and then green by mineral

acids. A *monohydrate* can also be obtained. A. Werner and co-workers obtained the anhydrous *dextro-salt*, and *laevo-salt* by treating an ice-cold soln. of the  $\mu$ -amino-peroxy-quaterethylenediaminebromide with hydrobromic acid. The impure, reddish-brown crystalline powder can be purified by converting it into the dithionate and rubbing up the product with sodium bromide and water, washing the pale red, crystalline powder with alcohol and ether, and drying it over calcium chloride. The sp. rotation of a 0.125 per cent. soln. of the *dextro-salt* is  $[\alpha] = 208^\circ$ .

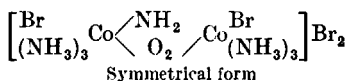
A. Werner and R. Feenstra obtained compounds which appeared to contain an imino-group, but, according to A. Werner, the question is an open one. By treating iminobispyridineoctamminotetrachloride with conc. hydrobromic acid, **cobaltic iminobispyridine-octamminotetrabromide**,  $[(\text{NH}_3)_4\text{py}.\text{Co}(\text{NH}_4\text{py})\text{Cl}_4]$ , was found in brown, acicular crystals; and by treating a soln. of diaquo- $\mu$ -amino-ol-hexamminonitrate with hydrobromic acid, A. Werner and F. Steinitzer obtained a dirty green powder of **cobaltic iminohexamminobromide**,  $\text{Co}(\text{NH}_3)_6(\text{NH})\text{Br}_4$ , but its nature has not yet been established.

There is also the black, crystalline powder, **cobaltic diozo-trimidodexamminobromide**,  $(\text{O}_3)_2(\text{NH})_3\text{Co}_4(\text{NH}_3)_{16}\text{Br}_8 \cdot \text{H}_2\text{O}$ , prepared by A. Werner and co-workers by the action of hydrobromic acid on the nitrate. Its constitution has not been established.

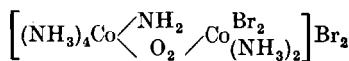
A. Werner and F. Beddow,<sup>12</sup> and A. Werner and A. Grün obtained **cobaltic  $\mu$ -amino-peroxy-octamminobromide**,  $[(\text{NH}_3)_4\text{Co}=(\text{NH}_2)\text{O}_2\cdots\text{Co}(\text{NH}_3)_4]\text{Br}_4 \cdot \text{H}_2\text{O}$ , by triturating G. Vortmann's sulphate—*vide supra*, the corresponding chloride—with conc. hydrobromic acid; or by similarly treating the sulphate of the series. The microcrystalline powder consists of green prisms. The aq. soln. of the salt decomposes rapidly.

A. Werner and co-workers<sup>13</sup> prepared **cobaltic  $\mu$ -amino-peroxy-quaterethylenediaminebromide**,  $[\text{en}_2\text{Co}=(\text{NH}_2)\text{O}_2\cdots\text{Co en}_2]\text{Br}_4 \cdot 6\text{H}_2\text{O}$ , by treating a cold, sat. soln. of the corresponding nitrate with ammonium bromide. The cubic crystals of the *hexahydrate* appear almost black in reflected light, and yellowish-green in transmitted light. The salt becomes anhydrous at  $110^\circ$ . The aq. soln. is yellowish-green, and it has a neutral reaction. J. Angerstein, and A. Gordienko studied the absorption spectra of aq. soln. The *dextro-salt*, and the *laevo-salt* can be obtained from the corresponding camphor bromosulphonates. The greenish-black, prismatic crystals, in 0.125 per cent. aq. soln., have the sp. rotations  $[\alpha] = 840^\circ$  for *dextro-salt*, and  $-840^\circ$  for the *laevo-salt*.

A. Werner<sup>14</sup> prepared **cobaltic dibromo- $\mu$ -amino-peroxy-hexamminobromide**, in *symmetrical* and *asymmetrical* forms:



Symmetrical form



Asymmetrical form

The symmetrical variety was obtained by the action of conc. hydrobromic acid on a warm, aq. soln. of  $\mu$ -amino-peroxy-ol-hexamminobromide; the small, greenish-black crystals are sparingly soluble in water. The asymmetrical form was prepared by the action of ammonium bromide on the asymmetrical chloride. The dark brown crystals are easily soluble in water, and pass into  $\mu$ -amino-peroxy-octamminobromide when treated with liquid ammonia. A. Werner and A. Baselli<sup>15</sup> found that **cobaltic  $\mu$ -amino-ol-octamminobromide**,  $[(\text{NH}_3)_4\text{Co}=(\text{NH}_2)(\text{OH})\cdots\text{Co}(\text{NH}_4)_4]\text{Br}_4 \cdot 4\text{H}_2\text{O}$ , separates out when an aq. soln. of bromoaquo- $\mu$ -amino-octamminobromide is allowed to stand for some time, and the same salt is produced when the sulphate is rubbed up with conc. hydrobromic acid, and the product crystallized from water acidulated with acetic acid. The garnet-red, prismatic crystals of the *tetrahydrate* effloresce over sulphuric acid; at  $60^\circ$ , and over phosphorus pentoxide, all 4 mols. of water are given off. Water dissolves about 1.3 per cent. of the salt; and conc. hydrobromic acid converts it into bromoaquo- $\mu$ -amino-octamminobromide. A. Werner prepared dark red crystals of **cobaltic  $\mu$ -amino-ol-quaterethylenediaminebromide**,  $[\text{en}_2\text{Co}=(\text{NH}_2)(\text{OH})\cdots\text{Co en}_2]\text{Br}_4 \cdot 4\text{H}_2\text{O}$ , in dark red crystals, by triturating the iodide with ammonium bromide.

A. Werner<sup>16</sup> prepared **cobaltic triol-hexamminobromide**,  $[(\text{NH}_3)_3\text{Co}\cdots(\text{OH})_3]$



$\text{Co}(\text{NH}_3)_3\text{Br}_3$ , by warming 10 grms. of bromochloroaquotriamminobromide with 50 c.c. of water for a few minutes at  $60^\circ$ . The salt forms red, acicular prisms. The sat., aq. soln. has 7.7 per cent. of the salt at room temp. The aq. soln. is decomposed by heat. G. R. Mines studied the physiological action.

A. Werner, and I. Fürstenberg obtained **cobaltic  $\mu$ -amino-diol-hexamminobromide**,  $[(\text{NH}_3)_3\text{Co} \equiv (\text{NH}_2)(\text{OH})_2 \text{Co}(\text{NH}_3)_3]\text{Br}_3$ , by treating a warm soln. of diaquo- $\mu$ -amino-ol-hexamminonitrate with ammonium bromide; or by triturating the corresponding iodide with silver bromide. The small, needle-like crystals are sparingly soluble in cold water, and the aq. soln. has a neutral reaction. A. Werner, and A. Werner and F. M. Grigorieff prepared cobaltic- $\mu$ -amino-peroxo-ol-hexammine, and A. Werner and F. M. Grigorieff prepared **cobaltic  $\mu$ -amino-peroxo-ol-hexamminobromide**,  $[(\text{NH}_3)_3\text{Co} \equiv (\text{NH}_2)(\text{OH})\text{O}_2 \text{Co}(\text{NH}_3)_3]\text{Br}_3 \cdot 2\text{H}_2\text{O}$ —*vide supra*, the corresponding chloride. The black chloride is triturated with a conc. soln. of silver nitrate, and when the filtrate is saturated with ammonium bromide, dark green crystals of the *dihydrate* are formed. The aq. soln. has a neutral reaction. The salt is reduced by sulphurous acid to a  $\mu$ -amino-diol-hexammino-salt.

A. Werner<sup>17</sup> prepared **cobaltic hexol-hexamminobromide**,  $[(\text{NH}_3)_3\text{Co} \equiv (\text{OH})_3 \text{Co} \equiv (\text{OH})_3 \text{Co}(\text{NH}_3)_3]\text{Br}_3$ , by treating 2 grms. of the corresponding chloride with 1 c.c. of conc., aq. ammonia, and 80 c.c. of water, and adding ammonium bromide to the rapidly-filtered liquid. The small, brown, scaly crystals are washed with alcohol and ether.

A. Werner<sup>18</sup> obtained **cobaltic hexol-dodecamminobromide**,  $[\text{Co}\{(\text{OH})_2 = \text{Co}(\text{NH}_3)_4\}_3]\text{Br}_6 \cdot 8\text{H}_2\text{O}$ , by heating dibromotetramminobromide with a little water, and filtering rapidly, when the soln., almost black, deposits black, tabular crystals. It is also obtained by precipitation from a soln. of another salt of the series by means of sodium bromide. It can be re-crystallized from conc. acetic acid, and washed with alcohol and ether. When air-dried, the product is the *octohydrate*. A. Werner also prepared the *dextro-salt*, and the *laevo-salt* by adding sufficient silver camphorbromosulphonate to precipitate all the chlorine, and then treating the soln. with dil. acetic acid. The first crops of crystals of the *d*-camphorbromosulphonate are usually *laevo*-rotatory, and those of the *l*-camphorbromosulphonate, *dextro*-rotatory. The active bromides were prepared by dissolving these salts in just sufficient aq. acetone (50 per cent.), adding small quantities of sodium bromide until the precipitate had a marked activity, and then diluting the mother-liquor with absolute alcohol. The *dextro*- and *laevo*-bromides crystallized as *dihydrates*. The 0.05 per cent. soln. in 1:1 aqueous acetone, and  $\lambda = 560$ , had the sp. rotations  $[\alpha] = 1050^\circ$  for the *dextro-salt*, and  $-4500^\circ$  for the *laevo-salt*. The anomalous dispersion was studied by A. Werner, and J. Lifschitz. A. Werner prepared **cobaltic hexol-sexiesethylenediamineobromide**,  $[\text{Co}\{(\text{OH})_2 = \text{Co}(\text{en})_2\}_3]\text{Br}_6$ , by treating a conc. soln. of the nitrate with sodium bromide. The reddish-brown, acicular crystals are freely soluble in water. Cobaltic hydroxide separates from the boiling, aq. soln.; hydrobromic acid converts it into green trans-dibromobisethylene-diaminebromide.

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## § 20. Cobaltous Iodide

O. L. Erdmann<sup>1</sup> obtained **cobaltous iodide**,  $\text{CoI}_2$ , by heating powdered cobalt and iodine in a glass tube, and added that the resulting product is greyish-green, without metallic lustre, and fuses when heated, but does not sublime. It is also obtained by heating cobalt in a current of iodine vapour. W. Biltz and E. Birk obtained the iodide by heating spongy cobalt—obtained by heating the oxalate in hydrogen—in a current of hydrogen iodide below the m.p. of cobalt iodide,  $400^\circ$  to  $500^\circ$ , then raising the temp. to about  $550^\circ$ , when the iodide melts, and finally cooling in vacuo, so as to remove the absorbed gases. W. N. Hartley, and A. Étard dehydrated the hexahydrate by keeping it in a vacuum over conc. sulphuric acid for 5 or 6 days; W. N. Hartley, by heating the hexahydrate to  $130^\circ$ ; and A. Ferrari and F. Giorgi, by drying and melting the hexahydrate in a current of hydrogen and hydrogen iodide. C. F. Rammelsberg, and O. L. Erdmann obtained an aq. soln. of the salt by placing the finely-divided metal in contact with iodine and water, when the temp. rises and a red liquid is formed. I. Bolschakoff observed that if the aq. soln. be evaporated and then cooled, crystals of the *hexahydrate*,  $\text{CoI}_2 \cdot 6\text{H}_2\text{O}$ , are formed as red, hexagonal prisms—W. N. Hartley recommended cooling the liquid to about  $16^\circ$ ; a further concentration and cooling of the soln., by a freezing mixture, yields the *enneahydrate*,  $\text{CoI}_2 \cdot 9\text{H}_2\text{O}$ , which forms red, rhombic plates; and these crystals, at  $6.4^\circ$ , form the hexahydrate. A. Étard obtained the *tetrahydrate*,  $\text{CoI}_2 \cdot 4\text{H}_2\text{O}$ , in green plates from hot, conc. soln.; and W. N. Hartley, and C. F. Rammelsberg obtained the green *dihydrate*,  $\text{CoI}_2 \cdot 2\text{H}_2\text{O}$ , by evaporating a conc. soln. of the salt over sulphuric acid.

According to W. Biltz and E. Birk, the vapour of ordinary cobalt iodide in vacuo, partly condenses as iodine, and partly as an ochre-yellow sublimate of unstable  **$\beta$ -cobalt iodide**; the ordinary black, stable form is  **$\alpha$ -cobalt iodide**. The sp. gr. of the  $\beta$ -iodide is 5.45 at  $25^\circ/4^\circ$ , being rather less than that of the  $\alpha$ -iodide. When the yellow  $\beta$ -iodide is heated to  $400^\circ$ , it forms the black  $\alpha$ -iodide. The  $\alpha$ -iodide forms a rose-red soln. when dissolved in water, but the aq. soln. of the  $\beta$ -iodide is pale wine-yellow, and the soln. is almost colourless if free iodine has been removed by chloroform. The aq. soln. of the  $\beta$ -iodide is stable for about a day, and with warming or concentration in vacuo, it becomes rose-red. Both the rose-red and the pale yellow soln. have the same electrical conductivities.

Ordinary cobalt iodide,  $\alpha$ -iodide, is black; and, according to A. Hantzsch, the

greenish colour which it usually appears to have, is due to the presence of a little free iodine. The crystals are hexagonal, and A. Ferrari and F. Giorgi observed that the space-lattice is of the cadmium iodide type, with  $a=3.96$  A.,  $c=6.65$  A., and  $a:c=1:1.68$ . W. Biltz and E. Birk gave 5.584 for the sp. gr. at  $25^\circ/4^\circ$ ; and G. L. Clark and H. K. Buckner gave 5.68—A. Ferrari and F. Giorgi calculated 5.75 from the X-radiograms. W. Biltz and E. Birk gave 56.02 for the mol. vol., and the subject was discussed by F. Ephraim, and F. Ephraim and O. Schütz. G. L. Clark and H. K. Buckner gave 2.90 for the sp. gr. of the hexahydrate, and said that there is an 11.2 per cent. contraction in the reaction:  $\text{CoI}_2 + 6\text{H}_2\text{O} = \text{CoI}_2 \cdot 6\text{H}_2\text{O}$ . G. Devoto and A. Guzzi gave  $495^\circ$  for the m.p., but W. Biltz and E. Birk gave  $515^\circ$  to  $520^\circ$  in vacuo, and A. Ferrari and F. Giorgi,  $515^\circ$  in a current of iodine. I. Bolschakoff found the enneahydrate passes into the hexahydrate at  $6.4^\circ$ ; W. N. Hartley said that the hexahydrate loses its water slowly in vacuo over sulphuric acid, or rapidly at  $130^\circ$ . The iodide begins to lose iodine at about  $540^\circ$ , and it boils at  $570^\circ$  to  $575^\circ$  with the dissociation of part of the iodide into iodine and cobalt. Some  $\beta$ -iodide is formed as a sublimate. K. Jellinek and R. Ulroth found the partial press. of the iodine at  $535^\circ$ ,  $605^\circ$ , and  $685^\circ$  to be, respectively,  $P_{\text{I}_2}=1.91 \times 10^{-3}$ ,  $6.76 \times 10^{-3}$ , and  $2.57 \times 10^{-2}$ . W. Geller measured the vap. press. of aq. soln. G. Devoto and A. Guzzi gave for the heat of formation from gaseous iodine ( $\text{Co, I}_2$ ) = 39.13 Cals.; W. Biltz, ( $\text{Co, I}_2, \text{Aq.}$ ) = 57 Cals.; and M. Berthelot, and L. Pigeon, 54.3 Cals. With iodine in soln., J. Thomsen gave ( $\text{Co, I}_2, \text{Aq.}$ ) = 42.52 Cals.; L. Pigeon, 41.5 Cals.; and M. Berthelot, 40.7 Cals. G. Devoto and A. Guzzi gave 18 Cals. for the heat of soln. of a mol of the anhydrous iodide in 1900 mols of water at  $18^\circ$ ; and A. Mosnier, 18.8 Cals. F. Ephraim and O. Schütz, and E. Rabinowitsch and E. Thilo discussed the heats of formation of the halides of the cobalt family. G. Devoto and A. Guzzi calculated for the free energy of formation of the molten salt, 13,800 cal.

H. Fesefeldt measured the absorption spectrum of thin films of the iodide. A. Étard observed that between  $-22^\circ$  and  $20^\circ$ , the aq. soln. is dark red; at higher temp., it becomes olive-green; and above  $35^\circ$ , green. Observations on the colour and absorption spectrum were made by W. Ackroyd, W. R. Brode and R. A. Morton, W. R. Brode, F. L. Cooper, G. Denigès, and R. A. Houstoun and co-workers.

W. Riedel found the electrical conductivity of soln. with a mol of the iodide, in  $v$  litres, at  $25^\circ$ :

$v$	$20^\circ$	$80^\circ$	$320^\circ$	$1280^\circ$	$5120^\circ$
$\mu$					
$\nu$	99.02	109.03	116.15	121.50	127.93
$\alpha$	0.77	0.85	0.90	0.94	0.995

The limiting value at infinite dilution is 128.61. The calculated degrees of ionization,  $\alpha$ , are indicated above; the transport numbers for the anion for  $v=20.8$ , 203.5, and 432, at  $18^\circ$ , are, respectively, 0.6218, 0.6062, and 0.6040; and for the cations, 0.3782, 0.3938, and 0.3960. The degrees of the hydrolysis for soln. with 0.05 and 0.01 mol per litre, are, respectively, 0.05 and 0.11 per cent., and the  $\text{H}^+$ -ion concentration, respectively,  $10^{-4.90}$ , and  $10^{-4.95}$ . G. Dickhaus gave for a soln. of 0.0158 grm. of  $\text{CoI}_2$  in 100 c.c. of water, at different temp:

	$33^\circ$	$34^\circ$	$37^\circ$	$38^\circ$	$46^\circ$	$47^\circ$
Conductivity .	184.935	181.475	172.406	169.168	148.460	145.973

There are irregularities between  $33.6^\circ$  and  $33.7^\circ$ , between  $37.7^\circ$  and  $37.8^\circ$ , and between  $46.2^\circ$  and  $46.3^\circ$ ; irregularities were also observed by J. Hamacher between  $24^\circ$  and  $25^\circ$ , between  $39^\circ$  and  $41^\circ$ , between  $35^\circ$  and  $39^\circ$ , and between  $40^\circ$  and  $42^\circ$ . P. Walden measured the conductivity of soln. of the salt in phosphoryl chloride. G. Devoto and A. Guzzi found the decomposition potential of the molten iodide is 0.872 volt at  $700^\circ$ , 0.802 volt at  $750^\circ$ , 0.704 volt at  $800^\circ$ , and 0.590 volt at  $850^\circ$ . W. Riedel gave for the e.m.f. of the cell  $\text{Pt}(\text{H}_2) | \text{CoI}_2 | \text{KCl}_{\text{sat. soln.}} | 0.1N\text{-KCl, Hg}_2\text{Cl}_2 | \text{Hg}$ , with the cobalt iodide soln. containing 0.05 and 0.01 mol. per litre, respectively, 0.6270 and

0.630 volt. G. Tammann and H. O. von Samson-Himmelsjerna studied the potential of cobalt in soln. of the iodide. W. Klemm and W. Schüth found the magnetic susceptibilities at 91° K., 195° K., 293° K., 513° K., and 673° K. to be, respectively,  $\chi \times 10^6 = 100, 51.4, 34.4, 19.4$ , and 14.6. O. Liebknecht and A. P. Wills found the magnetic susceptibility of an aq. soln. to be  $33 \times 10^{-6}$  mass unit at 18°.

Cobalt iodide is reduced to the metal when heated in hydrogen. K. Jellinek and R. Ulroth found that in the balanced reaction:  $\text{CoI}_2 + \text{H}_2 \rightleftharpoons \text{Co} + 2\text{HI}$ , the equilibrium constant,  $P_{\text{HI}}^2/P_{\text{H}_2}$ , is 0.30, 0.57, and 1.21, respectively, at 535°, 605°, and 685°. According to A. Étard, the percentage solubility,  $S$ , of the salt in water, is:

	-22°	-8°	-2°	9°	25°	46°	82°	111°	156°
$S$	52.4	56.7	58.7	61.4	66.4	79.0	80.7	80.9	83.1

A. Étard supposed the solid phase for the rose-red soln. below 20° to contain the hexahydrate; the mixed colour, olive-green between 20° and 35°, represented a mixture of the hexahydrate and the tetrahydrate; and the green colour above 35°, the tetrahydrate; and he found the solid phase above 46° to be the dihydrate. According to I. Bolschakoff, the transition temp. for the enne- and hexahydrates is 6.4°; and for the hexa- and tetrahydrates, 27°. C. F. Rammelsberg observed that cobalt iodide dissolves in a small proportion of water, forming a green soln., and with a larger proportion of water, a red soln. W. N. Hartley added that when the salt is dissolved in the smallest possible proportion of water, the soln. is red at -10°, and with a rising temp. the liquid passes through all shades of colour, from brown to olive-green, at 75°. The subject was discussed by J. H. Gladstone, and W. Ackroyd—*vide supra*, cobaltous chloride. W. N. Hartley observed that the hydrate, at 100°, loses nearly all its water, to form **cobalt oxyiodide**,  $\text{CoOI}_3$ , and C. F. Rammelsberg obtained what he regarded as a basic salt. By adding ammonia to a dil. soln. of cobalt iodide, a brown liquid is formed—presumably the peptized hydroxide—and a blue precipitate is produced which turns green when washed and dried. W. Riedel observed that cobaltous iodide unites with iodine to form a **cobaltous polyiodide**, possibly  $\text{CoI}_4$ , in aq. soln.; the conductivities corresponding with soln. containing a mol of the salt in  $v$  litres, at 25°, and the degrees of ionization,  $\alpha$ , are:

$v$	20	80	320	1280	5120	$\infty$
$\mu$	85.45	94.16	102.92	110.33	114.98	114.39
$\alpha$	0.745	0.821	0.899	0.962	1.000	—

R. F. Weinland and F. Schlegelmilch found that when a sat. soln. of cobaltous chloride is treated with iodine, dark orange-red crystals of **cobalt chloriodide**,  $\text{CoCl}_2 \cdot \text{ICl}_3 \cdot 8\text{H}_2\text{O}$ , are formed. The iodine chloride can be extracted with carbon tetrachloride. P. Walden observed that the iodide forms a violet soln. with thionyl chloride; and a yellowish-brown soln. with selenium monochloride. C. Dufraisse and D. Nakae studied the catalytic oxidation of sodium sulphite soln.; and A. Hantzsch and H. Carlsohn, the action of dil. sulphuric acid on the salt.

C. F. Rammelsberg found that when dry cobalt iodide is heated in dry ammonia, it swells up to form a red powder, **cobaltous hexamminoiodide**,  $\text{CoI}_2 \cdot 6\text{NH}_3$ , or  $[\text{Co}(\text{NH}_3)_6]\text{I}_2$ . W. Biltz could not obtain *cobalt decamminoiodide* analogous with the decamminochloride. C. F. Rammelsberg also described *cobaltous tetramminoiodide*,  $\text{CoI}_2 \cdot 4\text{NH}_3$ , said to be formed, in rose-red crystals, by cooling the violet liquid obtained by adding an excess of ammonia to a warm conc. soln. of cobalt iodide. W. Biltz and B. Fetkenheuer found that the product is the hexammine, not the tetrammine, and they modified the process by treating a hot, conc. soln. of cobalt iodide with conc. aq. ammonia until the precipitate which is first formed passes into soln., then adding air-free alcohol until a slight turbidity appears, cooling the soln., and washing the precipitate with conc. ammonia, and finally with alcohol. It is important to employ air-free liquids, since the iodide under these conditions is readily oxidized. The crystals are dark rose-red, with a yellow

tinge; the powder is pale rose-red. P. Stoll found that the X-radiograms correspond with a cubic lattice of the calcium fluoride type. The elementary cube has the parameter  $A=10.92$ , and contains 4 mols. The arrangement is that indicated in connection with the corresponding chloride, Fig. 114. W. Biltz and E. Birk gave  $a=10.93$  A., and G. B. Naess and O. Hassel,  $a=10.91$  A., and 4.73 A. for the distance between the Co and I atoms. The subject was discussed by W. Biltz, and H. Hentschel and F. Rinne. W. Biltz and E. Birk gave 2.096 for the sp. gr. at  $25^\circ/4$ , and 198.0 for the mol. vol.; G. L. Clark and H. K. Buckner gave 2.36 for the sp. gr. The mol. vol. of the  $\text{NH}_3$ -groups was also discussed by W. Hieber and E. Levy, W. Biltz and E. Birk, and W. Biltz. F. Ephraim found for the dissociation press.,  $p$  mm., of the ammonia:

	143.5°	163°	170°	174.5°	184.5°	188.5°	193°	197.5°
$p$	92	182	245	292	440	515	605	730

and the results are indicated in Fig. 114. W. Biltz and B. Fetkenheuer said that the results of W. Peters are too low. W. Biltz and G. F. Hüttig found that the

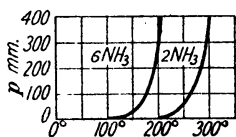


FIG. 114.—Dissociation Pressures of the Cobalt Amminiodides.

dissociation temp. at 100 mm. press. is  $141^\circ$ . The heat of formation from cobaltous iodide is 16.43 Cals. per mol of  $\text{NH}_3$ . The subject was discussed by W. Biltz and co-workers, G. L. Clark, and by F. Ephraim. When the hexammine is heated to  $156^\circ$ , and the containing vessel repeatedly evacuated, it passes into **cobaltous diamminiodide**,  $\text{CoI}_2 \cdot 2\text{NH}_3$ . This dark blue variety is considered to be the *stable* or  $\alpha$ -form, or *cis*-form as contrasted with the malachite-green salt or *unstable* or  $\beta$ -form, or *trans*-form which is obtained when the hexammine is heated at  $92^\circ$ , in vacuo, over sulphuric acid. The  $\beta$ -form is more readily decomposed by exposure to air than is the case with the  $\alpha$ -form; and the  $\beta$ -form passes into the  $\alpha$ -form when it is heated. The diammine forms solid soln. with the hexammine. The dissociation press. at  $136.5^\circ$  was 0.17 mm., and at  $153.5^\circ$ , 0.94 mm. The decomposition temp. for 100 mm. press. is  $272^\circ$ . The salt melts at  $222^\circ$ . W. Biltz and co-workers found that the heat of formation is 10.17 Cals. per mol of  $\text{NH}_3$ . The subject was discussed by G. L. Clark, and W. Hieber and E. Levy; and the magnetic susceptibility, by W. Klemm and W. Schüth. In attempting to prepare **cobaltous monamminiodide**,  $\text{CoI}_2 \cdot \text{NH}_3$ , by heating a mixture of cobalt iodide and hexamminiodide, in theoretical proportions, only a mixture of cobalt iodide and diamminiodide was formed. According to H. Franzen and H. L. Lucking, when conc. soln. of cobalt iodide and hydrazine iodide are mixed, a rose-red, crystalline powder of **cobaltous dihydraziniodide**,  $\text{CoI}_2 \cdot 2\text{N}_2\text{H}_4$ , is formed. The chlorides and bromides under similar conditions furnish double salts. A better yield is obtained by mixing aq. soln. of cobalt iodide and hydrazine hydrate. The product is sparingly soluble in water, and freely soluble in acids.

According to P. Walden, cobalt iodide is soluble in **phosphoryl chloride**, and in **arsenic trichloride**, but nearly insoluble in **arsenic tribromide**. O. L. Erdmann said that cobalt iodide is readily soluble in **ethyl alcohol**; forming a blue soln. studied by W. R. Brode, F. L. Cooper, and A. Hantzsch and H. Carlsohn; the blue soln. formed with **ether** was studied by A. Hantzsch, and A. Hantzsch and H. Carlsohn. W. Eidmann, and A. Naumann found that the iodide is soluble in **acetone**; and A. Naumann, that it is soluble in **methyl acetate**. P. Walden measured the electrical conductivity of the soln. in **acetonitrile**. A. Naumann found that the soln. in **benzonitrile** is apple-green. P. Walden measured the conductivity of soln. in **methyl thiocyanate**, in **dimethyl sulphide**, and in **methyl sulphate**. B. Köhnlein observed no marked reaction with **propyl chloride**; F. Ephraim and R. Linn, and W. Hieber and co-workers studied the complex salt with **methylamine**, and also with **ethylamine**; F. Ephraim and R. Linn obtained no complex with **dimethylamine**; G. A. Barbieri and F. Calzolari, and F. Calzolari and U. Tagliavini obtained

complexes with **hexamethylenetetramine**; G. Spacu and G. Suci, and W. Hieber and co-workers with **ethylenediamine**; J. Frejka and L. Zahlova, with **diaminobutane**; W. Hieber and E. Levy, and W. Hieber and co-workers, with **aniline**; W. Hieber and co-workers, and R. Cernatescu and co-workers, with **phenylenediamine**; W. Hieber and F. Leutert, with **acetoxime**; F. Calzolari, with **caffein**; W. R. Brode, A. Hantzsch, W. Hieber and E. Levy, W. Hieber and F. Mühlbauer, W. Hieber and A. Woerner, A. Naumann and J. Schröder, E. G. V. Percival and W. Wardlaw, F. Schlegel, and R. F. Weinland and co-workers, with **pyridine**; E. G. V. Percival and W. Wardlaw, with **quinaldine**; and F. Blau, with **dipyridyl**, and with **phenanthroline**. E. Beckmann, and W. R. Brode observed that cobalt iodide is soluble in **quinoline**. M. R. Menz studied the complexes formed with **camphidine**; and A. Tettamanzi and B. Carli, with **triethanolamine**. C. Dufraisse and D. Nakae studied the catalytic action on the oxidation of **acraldehyde**, **benzaldehyde**, **furfuraldehyde**, **styrene**, and **turpentine**.

G. F. Campbell prepared **cesium cobaltous tetraiodide**,  $\text{Cs}_2\text{CoI}_4$ , from soln. of the component salts in the ratio  $\text{Cs} : \text{Co} = 1 : 4$  to 16. The green deliquescent crystals are whitened by decomposition when brought in contact with water or alcohol. Although **sodium cobaltous tetraiodide**,  $2\text{NaI}_2 \cdot \text{CoI}_2$ , has not been prepared, L. Cambi has obtained complexes with acetone, and acetic anhydride. A. Ferrari and A. Inganni observed that a continuous series of solid soln. is formed with cadmium and cobalt iodides, but no compound is formed. D. Dobroserdoff prepared **mercuric cobaltous hexaiodide**,  $2\text{HgI}_2 \cdot \text{CoI}_2 \cdot 6\text{H}_2\text{O}$ , in dirty red octahedra, by evaporating in vacuo a mixed soln. of the component salts. The crystals are like those of chrome alum; and A. Duboin likened them to those of the corresponding iron salt. The salt is decomposed by water; and it is soluble in alcohol, and acetone. D. Dobroserdoff also obtained **mercuric cobaltous tetraiodide**,  $\text{HgI}_2 \cdot \text{CoI}_2 \cdot 6\text{H}_2\text{O}$ , from the mother-liquor obtained in preparing the hexaiodide. The salt is not decomposed by water; F. Calzolari and U. Tagliavini obtained a complex salt with hexamethylenetetramine. A. Mosnier prepared **lead cobaltous hexaiodide**,  $\text{PbI}_2 \cdot 2\text{CoI}_2 \cdot 3\text{H}_2\text{O}$ , from soln. of the component salts; it is decomposed by water.

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## § 21. Cobaltic Iodide and its Complex Salts

The higher iodide of cobalt—cobaltic iodide,  $\text{CoI}_3$ —has not yet been isolated, but a remarkable number of stable complex salts of the ammine family has been prepared. The general properties are treated more fully in connection with the chlorides.

### *The $\text{CoA}_6$ or Hexammine Family.*

E. Frémy,<sup>1</sup> and O. W. Gibbs and F. A. Genth prepared cobaltic hexammino-iodide,  $[\text{Co}(\text{NH}_3)_6]\text{I}_3$ , by precipitation from a soln. of a cobaltic hexammino-salt

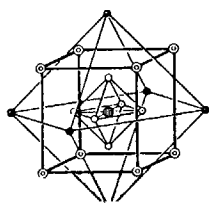


FIG. 115.—The Cobalt Atom and its Surroundings.

by a soln. of potassium iodide. S. M. Jørgensen obtained it by adding hydriodic acid to a soln. of the hexamminohydroxide. The orange-red to garnet-red crystals are hexakisoctahedra belonging to the cubic system, and they were described by F. M. Jäger, and W. Nowaki. The X-radiograms obtained by K. Meisel and W. Tiedje furnished data from which they derived the following structure. Each cobalt atom is surrounded by six nitrogen atoms of the six  $\text{NH}_3$ -groups arranged at the apices of an octahedron, Fig. 115, so that the distances between the cobalt and nitrogen atoms are 1.9 Å. These distances are exaggerated in Fig. 116. The cobalt atoms are also surrounded by two sets of iodine atoms—(i) eight iodine atoms of the first kind are arranged at the apices of a cube and at a distance of 4.7 Å. from the cobalt atom; and (ii) six iodine atoms of the second kind are arranged at the apices of another octahedron at a distance of 5.45 Å. from the cobalt atom. This gives a kind of structure which is a combination of the sodium chloride, and the calcium fluoride lattices. Each cobalt atom is arranged in the lattice as indicated in

Figs. 116 and 117. The systems about the different cobalt atoms, Fig. 115, belong in part to other cobalt atoms, and likewise also with the elementary cells, Figs. 116 and 117. As a result, there are, on the average, four  $[\text{Co}(\text{NH}_3)_6]\text{I}_3$ -molecules per unit cell. The face-centred, cubic cells have an edge of length  $a=10.91 \text{ \AA}$ . R. W. G. Wyckoff and T. P. McCutcheon, G. Natta, O. Hassel and

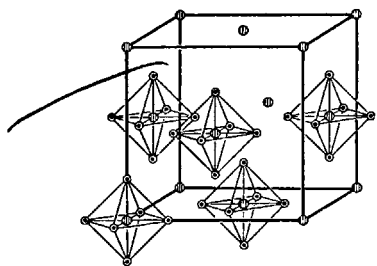


FIG. 116.—The Arrangement of the Cobalt Atoms in the Lattice; and of the  $\text{NH}_3$ -groups about each Cobalt Atom.

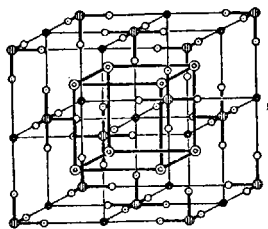


FIG. 117.—The Arrangement of the Different Atoms in the Face-centred Lattice.

G. B. Naess, and O. Hassel gave  $a=10.88 \text{ \AA}$ ; H. Hentschel and F. Rinne,  $10.91 \text{ \AA}$ ; and P. Stoll,  $10.92 \text{ \AA}$ . Whilst K. Meisel and W. Tiedje calculated  $1.9 \text{ \AA}$  for the parameter between the Co and N-atoms, R. W. G. Wyckoff and T. P. McCutcheon gave  $2.2 \text{ \AA}$ ; H. Hentschel and F. Rinne,  $1.64$  to  $1.91 \text{ \AA}$ ; and P. Stoll,  $4.1 \text{ \AA}$ . G. B. Naess and O. Hassel studied the lattice structure. G. Natta gave for the calculated sp. gr.,  $2.83$ ; F. M. Jäger found the sp. gr. to be  $2.526$  at  $15^\circ$ ; the mol. vol.,  $214.52$ ; and the topic axial ratios  $\chi : \psi : \omega = 5.9864 : 5.9864 : 5.9865$ . W. Biltz and E. Birk, found the sp. gr. to be  $2.746$  at  $25^\circ/4$ , and its mol. vol.  $197.3$ ; and F. Ephraim and O. Schütz, sp. gr.  $2.636$  at  $25^\circ$ , and mol. vol.,  $205.6$ . W. Biltz calculated the mol. vol. of the  $\text{NH}_3$ -groups in the cobaltic hexamminoiodide to be  $19$ , whereas for the corresponding cobaltous salt it is  $24$ . Observations on the subject were also made by R. Klement, and E. Birk; and W. Biltz, E. Feytis, and L. C. Jackson studied the magnetic properties. P. Pascal, and E. Rosenbohm gave for the magnetic susceptibility,  $-0.323 \times 10^{-6}$  mass unit.

S. M. Jørgensen found the iodide to be less soluble in water than the bromide. F. Ephraim and co-workers, and P. Mosimann observed that a sat., aq. soln., at  $18^\circ$ , contains  $0.015$  mol or  $0.819$  grm. per litre. F. Ephraim and P. Mosimann prepared a polyiodide, **cobaltic hexamminoenneaiodide**,  $[\text{Co}(\text{NH}_3)_6]\text{I}_3.3\text{I}_2$ , by the action of a soln. of iodine in potassium iodide on the hexamminochloride. When the brown needles are extracted with carbon disulphide, two-thirds of the iodine is removed. F. Ephraim found that when the hexamminoiodide is treated with liquid ammonia, or with gaseous ammonia at  $-21^\circ$ , a reddish-yellow **cobaltic hexadecamminoiodide**,  $[\text{Co}(\text{NH}_3)_6]\text{I}_3.10\text{NH}_3$ , is formed, and this compound, at  $-15.5^\circ$ , yields **cobaltic enneamminoiodide**,  $[\text{Co}(\text{NH}_3)_6]\text{I}_3.3\text{NH}_3$ ; and at  $14^\circ$ , **cobaltic heptamminoiodide**,  $[\text{Co}(\text{NH}_3)_6]\text{I}_3.\text{NH}_3$ , which has a dissociation temp. of  $45.5^\circ$ . F. Ephraim and co-workers obtained reddish-brown crystals of **mercuric cobaltic hexamminopentaiodide**,  $[\text{Co}(\text{NH}_3)_6]\text{I}_3.\text{HgI}_2$ , of sp. gr.  $3.550$  at  $25^\circ$ , and mol. vol.  $280.7$ ; also **mercuric cobaltic hexamminoenneaiodide**,  $[\text{Co}(\text{NH}_3)_6]\text{I}_3.3\text{HgI}_2.6\text{H}_2\text{O}$ , in small, reddish-brown crystals; and **bismuth cobaltic hexamminohexaiodide**,  $[\text{Co}(\text{NH}_3)_6]\text{I}_3.\text{BiI}_3$ , as a yellow precipitate. No **zinc cobaltic hexamminoiodide**, or **cadmium cobaltic hexamminoiodide** could be prepared, but stannous iodide with the hexamminoiodide forms brown crystals of presumably **stannous cobaltic hexamminoiodide**, which soon decompose. F. W. Bergstrom observed that no definite product is formed by the action of an ammonia soln. of potassium amide.

P. Pfeiffer and T. Gassmann,<sup>2</sup> and L. L. Lehrfeld heated cobaltic chloropentammino-chloride with 3 molar parts of monohydrated ethylenediamine until the mass became yellow, and then added potassium iodide to an aq. soln. of the product,

and obtained **cobaltic trisethylenediamineiodide**,  $[\text{Co en}_3]\text{I}_3 \cdot \text{H}_2\text{O}$ , in yellow crystals—the mother-liquid slowly deposited yellow, acicular crystals. F. M. Jäger prepared the same salt by the addition of potassium iodide to a soln. of the bromide, and in re-crystallizing the product from hot water, obtained dark red to reddish-brown crystals, which were rhombic bipyramids with the axial ratios  $a:b:c = 0.8700:1:1.7399$ , and had a sp. gr. of 2.270 at  $25^\circ/4^\circ$ . Observations on the crystals were also made by F. M. Jäger and P. Koets. J. Angerstein studied the absorption spectrum. P. Pfeiffer and T. Gassmann added that at  $16^\circ$  the aq. soln. contained 2.55 per cent. of the anhydrous iodide. A. Benrath and W. Kohlberg, and A. G. Bergmann found that the vap. press. measurements agreed with the existence of the *monohydrate*. P. Pfeiffer and M. Tilgner prepared **cobaltic trisethylene-diamineheptaoidide**,  $[\text{Co en}_3]\text{I}_3 \cdot 2\text{I}_2$ , in black, tabular or acicular crystals, by the heating of a soln. of the thiocyanate with an alcoholic soln. of iodine and potassium iodide, or by the action of a soln. of iodine and potassium iodide on the iodide. It forms yellow soln. with alcohol and pyridine; and is decomposed by dil. acids. G. Spacu and co-workers prepared **cobaltic trisethylenediaminechloroiodo-mercurate**,  $[\text{Co en}_3]\text{Cl}(\text{HgI}_4)$ ; and **cobaltic trisethylenediamineiodomercurate**,  $[\text{Co en}_3]\text{I}(\text{HgI}_4)$ .

F. M. Jäger prepared the *dextro-salt*, and the *lævo-salt* by treating the corresponding bromides with a conc. soln. of potassium iodide. The rhombic bipyramids of the *dextro-salt* have the axial ratios  $a:b:c = 0.8276:1:0.7386$ , and of the *lævo-salt*, 0.8256:1:0.7395. The sp. gr. are, respectively, 2.289 and 2.288 at  $25^\circ/4^\circ$ . E. Rosenbohm gave  $-3.84 \times 10^{-7}$  mass unit for the magnetic susceptibility of the *dextro-salt*. L. C. Jackson studied the magnetic properties; and F. M. Jäger, the optical properties. G. and P. Spacu prepared **silver cobaltic trisethylenediamineiodide**,  $[\text{Co en}_3](\text{AgI}_2)_2\text{I}$ ; and **lead cobaltic trisethylenediamineiodide**,  $[\text{Co en}_3](\text{PbI}_3)_3$ . C. S. Borzekowsky prepared the *dextro*- and *lævo*-forms of **cobaltic hydroxylaminebisethylenediamineamminioiodide**,  $[\text{Co}(\text{NH}_3)(\text{NH}_2\text{OH})\text{en}_2]\text{I}_3$ .

P. Pfeiffer and T. Gassmann obtained optically inactive, or racemic **cobaltic tripropylenediamineiodide**,  $[\text{Co pn}_3]\text{I}_3 \cdot \text{H}_2\text{O}$ , by adding potassium iodide to an aq. soln. of the corresponding chloride. F. M. Jäger and H. B. Blumendal prepared cobaltic triscyclopentanediamineiodide by the action of sodium iodide on a soln. of the chloride; and the *dextro-salt*, and *lævo-salt*, by the action of sodium iodide on soln. of the corresponding optically-active chlorides. The golden-yellow needles, according to E. Rosenbohm, have a magnetic susceptibility of  $-0.391 \times 10^{-6}$ . The magnetic properties were studied by L. C. Jackson. L. Tschugaëff and W. Sokoloff found that aq. soln., saturated at  $25^\circ$ , contains 5.98 per cent. of the iodide; and, according to P. Pfeiffer and T. Gassmann, one saturated at  $16^\circ$  contains 4.29 per cent. The salt is reprecipitated by potassium iodide; and potassium thiocyanate precipitates the corresponding thiocyanate. The *lævo-salt*, in brown needles, was prepared by L. Tschugaëff and W. Sokoloff by heating on a water-bath an aq. soln. of chloropentamminochloride and *l*-propyldiamine, and afterwards adding potassium iodide. An aq. soln. saturated at  $25^\circ$  contains 11.36 per cent. of the iodide—*i.e.* the solubility is nearly double that of the racemic salt. The sp. rotation of a 3.38 per cent. aq. soln. for Na-light is  $[\alpha] = 23.63^\circ$ . J. Frejka and L. Zahlova prepared **cobaltic trisbutylenediamineiodide**,  $[\text{Co bn}_3]\text{I}_3$ .

F. G. Mann and W. J. Pope obtained **cobaltic bistriaminopropanediamminioiodide**,  $[\text{Co}(\text{NH}_3)_2\text{ptn}_2]\text{I}_3$ , in orange-yellow needles by the action of potassium iodide on a soln. of the chloride. The salt is not decomposed at  $320^\circ$ , it is less soluble in water than the chloride; and it is not soluble in alcohol. F. G. Mann prepared **cobaltic bisdiaminodiethylenediaminotriiodide**,  $\text{Co}\{(\text{H}_2\text{N} \cdot \text{C}_2\text{H}_4)_2\text{NH}_2\}_2\text{I}_3$ . A. Werner and C. Kreutzer, and A. Werner and R. Samanek prepared **cobaltic cis-bisethylenediaminediamminioiodide**,  $[\text{Co}(\text{NH}_3)_2\text{en}_2]\text{I}_3$ , by the action of potassium iodide on a soln. of the nitrate at  $60^\circ$ . The garnet-red, rhombic plates are strongly refractive; 5.6 parts of water dissolve 1 part of the iodide at  $23^\circ$ . A. Werner and Y. Shibata prepared the *dextro-salt*, and the *lævo-salt*, in dark yellow needles by the action of ammonium iodide on the corresponding bromides. The sp. rotation for the *dextro-salt* is  $[\alpha] = 29^\circ$ , and for the *lævo-salt*,  $-28^\circ$ . A. Werner and R. Samanek also prepared **cobaltic cis-bisethylenediaminediamminopolyiodide**. A. Werner and co-workers obtained **cobaltic trans-bisethylenediaminediamminioiodide**, in brownish-yellow plates by the action of potassium iodide on the corresponding chloride. One part of the iodide dissolves in 40.86 parts of water at  $23^\circ$ . A. Werner and K. Dawe reported **cobaltic bispropylenediaminediamminioiodide**,  $[\text{Co}(\text{NH}_3)_2\text{pn}_2]\text{I}_3 \cdot \text{H}_2\text{O}$ , by adding potassium iodide to a hot soln. of the corresponding chloride. The dark orange-red crystalline mass

gradually forms yellow needles. F. M. Jäger and H. B. Blumendal obtained **cobaltic ethylenediaminebis(cyclopentanediamine)iodide**,  $[\text{Co}(\text{C}_5\text{H}_{12}\text{N}_2)_2]\text{I}_3$ , in yellowish-brown needles, by fractional crystallization of the product of the action of sodium iodide on the corresponding chloride. P. Pfeiffer and T. Gassmann obtained **cobaltic propylenediamine-bisethylenediamineiodide**,  $[\text{Co}(\text{en}_2\text{pn})\text{I}_3 \cdot 3\frac{1}{2}\text{H}_2\text{O}]$ , in brownish-yellow needles, as in the case of the bromide. Water saturated at  $16^\circ$  contains 4.0 per cent. of the anhydrous salt. E. Rosenbohm said that the *dextro*-salt has a magnetic susceptibility of  $-0.385 \times 10^{-6}$ . L. C. Jackson studied the magnetic properties. F. M. Jäger and H. B. Blumendal prepared **cobaltic cis-bisethylenediaminecyclopentaneiodide**,  $[\text{Co}(\text{en}_2(\text{C}_5\text{H}_{12}\text{N}_2))\text{I}_3]$ , by treating the corresponding chloride with sodium iodide. The brownish-red, rhombic bipyramids have the axial ratios  $a : b : c = 1.7699 : 1 : 0.6494$ . They also prepared the *dextro*-salt, and the *laevo*-salt. F. M. Jäger obtained **cobaltic  $\alpha$ -phenanthrolinebisethylenediamineiodide**,  $[\text{Co}(\text{en}_2(\text{C}_{12}\text{H}_8\text{N}_2))\text{I}_3]$ , by the action of sodium iodide on the chlorosulphate. The dark brown, triclinic crystals have the axial ratios  $a : b : c = 0.6487 : 1 : 0.4692$ . He also prepared the *dextro*-salt, and the *laevo*-salt. R. Plischke, and W. A. Redeker prepared **cobaltic pyridine-bisethylenediamineamminiodide**,  $[\text{Co}(\text{NH}_3)(\text{en}_2\text{py})\text{I}_3]$ . F. M. Jäger and P. Koets obtained **cobaltic bistriaminotriethylaminesexiesethylenediamineiodide**,  $[\text{Co}_3(\text{en}_3(\text{C}_6\text{H}_{18}\text{N}_4))_2]\text{I}_3$ , by the action of sodium iodide on the chloride, or of barium iodide on the sulphate. The blood-red, acicular or columnar rhombic crystals have the axial ratios  $a : b : c = 0.6498 : 1 : 0.9959$ . The crystals are dichroic—blood-red and orange-yellow. C. J. Dippel, and J. M. Jäger prepared **cobaltic trisdiaminopentaneiodide**,  $[\text{Co}(\text{ptn}_3)\text{I}_3]$ , with  $\alpha\beta\delta$ - and  $\beta\beta\delta$ -diaminopentanes.

S. M. Jørgensen<sup>3</sup> prepared **cobaltic aquopentamminiodide**,  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{I}_3$ , by neutralizing an aq. soln. of the corresponding hydroxide or carbonate with dil. hydriodic acid, and precipitating the salt with the conc. acid; and F. Ephraim, by adding potassium iodide to a conc. soln. of the corresponding chloride. The dark red octahedra or six-sided plates were found by G. Natta to have a structure similar to that of the hexamminiodide. The face-centred, cubic lattice has 4 mols. per cell, and the parameter is  $a = 10.84 \text{ \AA}$ . Each cobalt atom is at the centre of an octahedron, the vertices of which are occupied by the  $\text{NH}_3$ - and  $\text{H}_2\text{O}$ -groups. The substitution of one of the  $\text{NH}_3$ -groups by a  $\text{H}_2\text{O}$ -group produces a slight contraction in the lattice, which otherwise remains unaltered. O. Hassel, and O. Hassel and G. B. Naess also found a contraction of the lattice from  $a = 10.88 \text{ \AA}$ . to  $a = 10.81 \text{ \AA}$ . by the replacement of the  $\text{NH}_3$ - by the  $\text{H}_2\text{O}$ -group. G. Natta calculated 2.81 for the sp. gr. F. Ephraim and O. Schütz gave 2.697 for the sp. gr. at  $25^\circ$ , and for the mol. vol. 201.3, corresponding with a vol. contraction of 55.8 per cent. in the formation of the compound. N. R. Dhar and G. Urbain measured the polarization tension—*vide* the hexamminochloride. P. Job studied the electro-metric titration of the soln. with silver nitrate.

S. M. Jørgensen observed that the iodide is less soluble than the bromide; and F. Ephraim and O. Schütz found that a sat. aq. soln. of the iodide has 0.155 mol per litre at  $17.5^\circ$ . S. M. Jørgensen said that at  $100^\circ$ , the aq. soln. in the presence of hydriodic acid, shows no inclination to pass into iodopentamminiodide. The aq. soln. gives no precipitate with hydrobromic acid, or with sodium dithionate, but precipitation occurs with potassium iodide, ferricyanide, chromate, and dichromate; dil. sulphuric acid forms an iodosulphate; hydrochloroplatinic acid gives a brown soln. which soon deposits platinic iodide. F. Ephraim found that at  $-18^\circ$  in ammonia gas, the product approximates to **cobaltic aquopentadecamminiodide**,  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{I}_3 \cdot 10\text{NH}_3$ , and as the temp. rises to  $56^\circ$ , all the ammonia is expelled. Various solid soln. are formed in between. F. Ephraim and P. Mosimann observed that neither **zinc cobaltic aquopentamminiodide**, nor **cadmium cobaltic aquopentamminiodide** is formed from a soln. of the component iodides, but yellowish-red needles of **mercuric cobaltic aquopentamminopentaidide**,  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{I}_3 \cdot \text{HgI}_2$ , are readily produced.

A. Werner prepared **cobaltic trans-aquobisethylenediamineamminiodide**,  $[\text{Co}(\text{NH}_3)(\text{en}_2(\text{H}_2\text{O}))\text{I}_3 \cdot \text{H}_2\text{O}]$ , in brownish-red prisms, by the action of potassium iodide on the corresponding bromide.

F. Ephraim reported **cobaltic diaquotetramminiodide**, probably  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{I}_3$ , to be formed in dark brown crystals with a violet tinge, by the action of potassium iodide on a soln. of the corresponding nitrate or chloride.

*The CoA<sub>5</sub> or Pentammine Family.*

A. Werner<sup>4</sup> prepared **cobaltic iodopentamminiodide**,  $[\text{Co}(\text{NH}_3)_5\text{I}]\text{I}_2$ , by heating the aquopentamminiodide between 60° and 80°; and also by rubbing up the nitrate of the series with potassium iodide. The olive-green, crystalline powder was found by R. Klement to have a sp. gr. of 2.926 at 25°/4°, and a mol. vol., 179.4. E. Birk, and W. Biltz discussed the mol. vol. of the contained  $\text{NH}_3$ -groups. F. Ephraim found that at 20° a litre of water dissolves 0.002 mol of the salt. The polarization tension was studied by N. R. Dhar and G. Urbain.

A. Werner obtained **cobaltic iodopentamminochloride**,  $[\text{Co}(\text{NH}_3)_5\text{I}]\text{Cl}_2$ , by rubbing up the nitrate with ammonium chloride and a little water, and then adding conc. hydrochloric acid to the cold aq. soln. The dark green, crystalline mass was found by R. Klement to have a sp. gr. 2.355 at 25°/4°, and a mol. vol. 145.2. The mol. vol. of the contained  $\text{NH}_3$ -groups was discussed by E. Birk, and W. Biltz. R. Ephraim observed that a sat., aq. soln. at 20° has 0.0154 mol per litre. The cold, aq. soln. was found by A. Werner to give precipitates with nitric and hydrobromic acids, and with potassium iodide, chromate, or dichromate, but not with sulphuric acid, sodium dithionate, ammonium sulphate or carbonate, or with potassium cyanide or thiocyanate. A. Werner prepared **cobaltic iodopentamminobromide**,  $[\text{Co}(\text{NH}_3)_5\text{I}]\text{Br}_2$ , in an analogous manner. The yellowish-green, crystalline powder was found by R. Klement to have a sp. gr. 2.926 at 25°/4°, and a mol. vol. 179.4. E. Birk, and W. Biltz discussed the mol. vol. of the contained  $\text{NH}_3$ -groups. F. Ephraim observed that a sat., aq. soln. has 0.00076 mol of the salt per litre at 20°.

F. Ephraim prepared **cobaltic bromopentamminiodide**,  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{I}_2$ , by the action of potassium iodide on the bromide of the series. The dark violet, tabular crystals were found by R. Klement to have a sp. gr. 2.721 at 25°/4°, and a mol. vol. 175.6; F. Ephraim and O. Schütz gave 2.665 for the sp. gr. at 25°, and 179.3 for the mol. vol. This corresponds with a vol. contraction of 55.8 per cent. in the formation of the salt. E. Birk, and W. Biltz discussed the mol. vol. of the contained  $\text{NH}_3$ -groups. F. Ephraim found that a sat., aq. soln. had 0.0101 mol per litre at 20°. J. N. Brønsted and co-workers discussed the solubility in water, and in methanol. E. Schmidt prepared **cobaltic bromoaquobisethylenediamineiodide**,  $[\text{Co}(\text{en}_2(\text{H}_2\text{O})\text{Br})\text{I}_2 \cdot \text{H}_2\text{O}]$ . C. S. Borzekowsky prepared the dextro- and lævo-forms of **cobaltic bromohydroxylaminebisethylenediamineiodide**,  $[\text{Co}(\text{NH}_2\text{OH})\text{en}_2\text{Br}]\text{I}_2$ .

S. M. Jörgensen obtained **cobaltic chloropentamminiodide**,  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{I}_2$ , by treating a soln. of the corresponding nitrate with potassium iodide; or the chloride with sodium iodide. R. Klement gave 2.502 for the sp. gr. at 25°/4°, and 173.3 for the mol. vol.; F. Ephraim and O. Schütz gave 2.417 for the sp. gr. at 25°, and 179.3 for the mol. vol. The vol. contraction in the formation of the compound was also studied by W. Biltz, and E. Birk. F. Ephraim observed that a sat., aq. soln. has 0.0418 mol per litre at 19°. J. N. Brønsted and co-workers discussed the solubility in water and in methanol. S. M. Jörgensen, and F. Ephraim and P. Mosimann described a **cobaltic chloropentamminopolyiodide**, prepared by the action of a soln. of iodine in hydriodic acid on the corresponding carbonate, or of a soln. of iodine and potassium iodide on the nitrate. F. Ephraim found that by treating the salt with ammonia at -21°, **cobaltic chlorohenamminiodide**,  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{I}_2 \cdot 6\text{NH}_3$ , is formed, and this, at -8°, passes into **cobaltic chlorohexamminochloride**,  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{I}_2 \cdot \text{NH}_3$ . F. Ephraim and P. Mosimann, and S. M. Jörgensen obtained **mercuric cobaltic chloropentamminotetraiodide**,  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{I}_2 \cdot \text{HgI}_2$ , in brown plates; S. M. Jörgensen, **mercuric cobaltic chloropentamminohexaiodide**,  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{I}_2 \cdot 2\text{HgI}_2$ , in sparingly soluble, brown needles; and F. Ephraim and P. Mosimann, **bismuth cobaltic chloropentamminooctoidide**,  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{I}_2 \cdot 2\text{BiI}_3$ , as a red, crystalline powder.

A. Werner and W. E. Boës obtained **cobaltic bromobisethylenediamineaminoiodide**,  $[\text{Co}(\text{NH}_3)_n\text{en}_2\text{Br}]\text{I}_2 \cdot \text{H}_2\text{O}$ , in reddish-brown needles, by the action of ammonium iodide on the corresponding dithionate. E. Berl prepared **cobaltic bromobisethylenediaminehydroxylamineiodide**,  $[\text{Co}(\text{NH}_2\text{OH})_n\text{enBr}]\text{I}_3$ . J. Meisenheimer and E. Kiderlen prepared **cobaltic chloroethylaminebisethylenediamineiodide**,  $[\text{Co en}_2(\text{C}_2\text{H}_5\text{NH}_2)\text{Cl}]\text{I}_2$ ; **cobaltic trans-chloroallylaminebisethylenediamineiodide**,  $[\text{Co en}_2(\text{C}_3\text{H}_5\text{NH}_2)\text{Cl}]\text{I}_2$ , in dark violet-red plates, sparingly soluble in water; **cobaltic chloroanilinebisethylenediamineiodide**,  $[\text{Co en}_2(\text{C}_6\text{H}_5\text{NH}_2)\text{Cl}]\text{I}_2$ , in reddish-brown prisms, decomposed at  $40^\circ$  to  $50^\circ$ ; **cobaltic chlorotoluidinebisethylenediamineiodide**,  $[\text{Co en}_2(\text{C}_6\text{H}_7\text{NH}_2)\text{Cl}]\text{I}_2$ , in reddish-brown, six-sided prisms which decompose at  $35^\circ$ ; and **cobaltic chlorobenzylaminebisethylenediamineiodide**,  $[\text{Co en}_2(\text{C}_6\text{H}_7\text{NH}_2)\text{Cl}]\text{I}_2$ , in raspberry-red needles. R. Vogel prepared **cobaltic chloropyridinebisethylenediamineiodide**,  $[\text{Co en}_2\text{py}]\text{Cl}]\text{I}_2$ .

G. T. Morgan and J. D. M. Smith<sup>5</sup> obtained **cobaltic hydroxypentamminoiodide**,  $[\text{Co}(\text{NH}_3)_5(\text{OH})]\text{I}_2$ , as a violet, crystalline powder, by treating the chloride with potassium iodide. M. Rosner obtained **cobaltic hydroxydipyridinetriamminoiodide**,  $[\text{Co}(\text{NH}_3)_3\text{Py}_2(\text{OH})]\text{I}_2$ . A. Werner prepared hydrated **cobaltic cis-hydroxyaquobisethylenediamineiodide**,  $[\text{Co en}_2(\text{H}_2\text{O})(\text{OH})]\text{I}_2$ . Brownish-red needles of the *monohydrate* are formed by adding pyridine to a dil. aq. soln. of the *cis*-diaquobisethylenediaminebromide, and then potassium bromide, and re-crystallizing the product from its aq. soln. R. Klement obtained the *dihydrate*, in small, brown crystals, by saturating with potassium iodide a cold, 10 per cent. aq. soln. of the corresponding phosphate. A. Werner obtained **cobaltic trans-hydroxyaquobisethylenediamineiodide**, by adding potassium iodide to an aq. soln. of a salt of the *trans*-diaquobisethylenediamine; or by heating *trans*-diaquobisethylenediaminechloride first with conc. potash-lye and then with potassium iodide. The reddish-brown plates are sparingly soluble in water.

#### *The CoA<sub>4</sub> or Tetrammine Family.*

H. J. S. King<sup>6</sup> prepared **cobaltic dihydroxytetramminoiodide**,  $[\text{Co}\{\text{Co}(\text{NH}_3)_4(\text{OH})_2\}_3]\text{I}_6$ . H. Seibt prepared **cobaltic cis-difluobisethylenediamineiodide**,  $[\text{Co en}_2\text{F}_2]\text{I}$ , as a red, crystalline powder, by the action of sodium iodide on a soln. of difluobisethylenediaminefluoride; and **cobaltic trans-difluobisethylenediamineiodide**, in green needles, by the action of ammonium iodide on the corresponding fluoride. A. Werner obtained **cobaltic cis-dichlorotetramminoiodide**,  $[\text{Co}(\text{NH}_3)_4\text{F}_2]\text{F}$ , in greyish-blue needles, by rubbing up the corresponding dithionate with ammonium chloride, and treating a soln. of the product with potassium iodide. The salt decomposes on keeping. A. Werner, and A. Werner and A. Klein prepared **cobaltic trans-dichlorotetramminoiodide** as a siskin-green, soluble powder by the action of potassium iodide on the corresponding hydrosulphate. The sp. gr. found by F. Ephraim and O. Schütz is 2.342 at  $25^\circ$ , the mol. vol. is 138.7, and the vol. contraction during the formation of the compound is 57.8 per cent. The aq. soln. decomposes in a short time. S. M. Jørgensen, P. Larisch, and A. Werner and P. Larisch prepared **cobaltic cis-dichlorobisethylenediamineiodide**,  $[\text{Co en}_2\text{Cl}_2]\text{I}$ , by adding potassium iodide to a sat., aq. soln. of the corresponding chloride. P. Larisch found that the dark violet, crystalline powder dissolves in 100 c.c. of water at  $1^\circ$ . S. M. Jørgensen, P. Larisch, and T. S. Price and S. A. Brazier prepared **cobaltic trans-dichlorobisethylenediamineiodide**, from the corresponding chloride, by the addition of potassium iodide. According to P. Larisch, 0.250 grm. of the green, tabular crystals dissolves in 100 c.c. of water at  $1^\circ$ . G. and P. Spacu prepared double salts: **cadmium cobaltic dichlorobisethylenediamineiodide**,  $[\text{Co en}_2\text{Cl}_2]_2\text{CdI}_4$ ; and **mercury cobaltic dichlorobisethylenediamineiodide**,  $[\text{Co en}_2\text{Cl}_2]_2\text{HgI}_3$ . C. Rix, and A. Werner prepared **cobaltic trans-dichloroethylenediaminediaminoiodide**,  $[\text{Co}(\text{NH}_3)_2\text{enCl}_2]\text{I}$ , as a green to brown precipitate, by adding potassium iodide to a cold, aq. soln. of the corresponding chloride. The powder is sensitive to light.

G. and P. Spacu prepared the **polyiodides**  $[\text{Co en}_2(\text{NO}_2)_2]\text{I}_4$ ;  $[\text{Co en}_2(\text{CNS})_2]\text{I}_3$ ;

$[\text{Co en}_2\text{Cl}_2]\text{I}_3$ ;  $[\text{Co en}_2\text{I}_2]\text{I}_3$ ;  $\text{Co}[\text{Co en}_2(\text{OH})_2]_3\text{I}_3$ ;  $\text{Co}[\text{Co en}_2(\text{OH})_2]_3\text{I}_6$ ; and  $[\text{Co en}_3]\text{I}_3$ .

A. Werner and A. Wolberg prepared **cobaltic trans-dibromotetramminoiodide**,  $[\text{Co}(\text{NH}_3)_4\text{Br}_2]\text{I}$ , in greenish-brown prisms, by the action of potassium iodide on the corresponding chloride. The salt is sparingly soluble in water, and it decomposes when kept for a long time. A. Werner obtained **cobaltic cis-dibromobis-ethylenediamineiodide**,  $[\text{Co en}_2\text{Br}_2]\text{I}$ , in scales resembling graphite, by adding potassium iodide to a soln. of the corresponding bromide. M. L. Ernsberger and W. R. Brode studied the absorption spectrum. A. Werner and A. Grün prepared **cobaltic bromochloroaquatrimminoiodide**, presumably  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})\text{ClBr}]\text{I} \cdot n\text{H}_2\text{O}$ , as a brown precipitate, by the action of potassium iodide on a soln. of the corresponding bromide; and similarly with **cobaltic bromochloroaquoethylenediamineamminoiodide**, presumably  $[\text{Co}(\text{NH}_3)\text{en}(\text{H}_2\text{O})\text{ClBr}]\text{I}$ .

#### *Complexes with Two or More Cobalt Atoms.*

G. Vortmann <sup>7</sup> prepared **cobaltic peroxo-decamminoiodide**,  $[\text{NH}_3)_5\text{Co}-\text{O}_2-\text{Co}(\text{NH}_3)_5]\text{I}_4$ , by adding potassium iodide to an oxidized ammoniacal soln. of cobaltous chloride; or by triturating the corresponding nitrate with a sat. soln. of potassium iodide. The small, green needles are stable in air; and sparingly soluble in water. They are decomposed, with the evolution of oxygen, by a large excess of water.

A. Werner and E. Kindscher prepared **cobaltic diol-octamminoiodide**,  $[(\text{NH}_3)_4\text{Co} \cdots (\text{OH})_2 \cdots \text{Co}(\text{NH}_3)_4]\text{I}_4 \cdot 2\text{H}_2\text{O}$ , by the action of potassium iodide on a soln. of the corresponding chloride. The dark violet crystals decompose above  $60^\circ$ ; they are coloured brown by exposure to air; and are readily dissolved by water. J. V. Dubsy and H. Frank, and H. Frank obtained **cobaltic diol-quaterethylenediamineiodide**,  $[\text{en}_2\text{Co} \cdots (\text{OH})_2 \cdots \text{Co en}_2]\text{I}_4$ , as a brownish-red, crystalline powder, by the action of potassium iodide on a soln. of the bromide.

A. Werner prepared **cobaltic  $\mu$ -amino-peroxo-quaterethylenediamineiodide**,  $[\text{en}_2\text{Co}=(\text{NH})_2\text{O}_2=\text{Co en}_2]\text{I}_3 \cdot 5\text{H}_2\text{O}$ , in small, brown needles, by rubbing up cobaltic  $\mu$ -amino-peroxo-quaterethylenediaminebromide with aq. ammonia and then adding sodium iodide; and also by rubbing up the corresponding dithionate with a soln. of potassium iodide. The salt is not precipitated from aq. soln. by potassium or ammonium bromide. The *dextro-salt* and the *laevo-salt* were obtained by A. Werner and co-workers from the corresponding  $\mu$ -amino-peroxo-salt, as above. The sp. rotation of 0.125 per cent. aq. soln. is  $[\alpha] = \pm 160^\circ$ .

A. Werner and F. Steinitzer obtained **cobaltic iminohexamminoiodide**,  $\text{Co}_2(\text{NH}_3)_6(\text{NH})\text{Cl}_4$ , by treating a warm, aq. soln. of diaquo- $\mu$ -amino-ol-hexammine-nitrate with hydriodic acid. The pale brown powder is sparingly soluble in cold water; and it is decomposed by warm water. A. Werner obtained **cobaltic  $\mu$ -amino-ol-quaterethylenediamineiodide**,  $[\text{en}_2\text{Co} \cdots (\text{NH}_2)(\text{OH}) \cdots \text{Co en}_2]\text{I}_4$ , as a pale red, crystalline powder, by the action of sodium iodide on an acetic acid soln. of  $\mu$ -amino-peroxo-quaterethylenediaminenitrate, adding sodium thiosulphate in excess, and salting out with sodium iodide. A. Werner obtained the *laevo-salt* from the corresponding  $\mu$ -amino-peroxo-nitrate, as just indicated.

A. Werner, and I. Fürstenberg prepared **cobaltic  $\mu$ -amino-diol-hexamminoiodide**,  $[(\text{NH}_3)_3\text{Co} \cdots (\text{NH}_2)(\text{OH})_2 \cdots \text{Co}(\text{NH}_3)_3]\text{I}_3$ , by the action of potassium iodide on a soln. of the bromide. The brownish-red needles are sparingly soluble in water, and the aq. soln. reacts neutral. The aq. soln. decomposes when heated.

A. Werner and G. Jantsch obtained **cobaltic diaquo-tetrol-quaterethylenediamineiodide**,  $[\text{en}_2\text{Co}=(\text{OH})_2 \cdots \text{Co}(\text{H}_2\text{O})_2 \cdots (\text{OH})_2=\text{Co en}_2]\text{I}_4 \cdot 2\text{H}_2\text{O}$ , by rubbing up a soln. of the sulphate with barium chloride, then with potassium iodide, and salting out the product from the aq. soln. by potassium iodide at  $30^\circ$ . The brownish-red powder is sparingly soluble in cold water, but readily soluble in hot water. It suffers no loss in weight over conc. sulphuric acid.

A. Werner prepared **cobaltic hexol-sexiesethylenediamineiodide**,  $[\text{Co}\{(\text{OH})_2 = \text{Co en}_2\}_3]\text{I}_6 \cdot 3\text{H}_2\text{O}$ , by the action of sodium iodide on a conc., aq. soln. of the corresponding nitrate. The violet-brown, crystalline powder is sparingly soluble in cold water, but it dissolves readily in hot water and at the same time is partially decomposed.

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## § 22. Cobalt Sulphides

M. von Orłowsky,<sup>1</sup> O. Schumann, E. Schürmann, E. F. Anthon, E. V. Britzke and A. F. Kapustinsky, G. Tamman and H. O. von Himmelstjerna, and

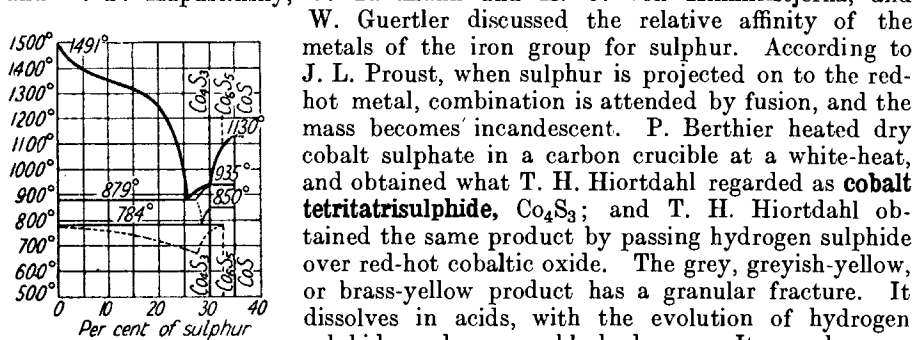


FIG. 118.—Freezing-point Curves of the System: Co-S.

W. Guertler discussed the relative affinity of the metals of the iron group for sulphur. According to J. L. Proust, when sulphur is projected on to the red-hot metal, combination is attended by fusion, and the mass becomes incandescent. P. Berthier heated dry cobalt sulphate in a carbon crucible at a white-heat, and obtained what T. H. Hiortdahl regarded as **cobalt tetratrisulphide**,  $\text{Co}_2\text{S}_3$ ; and T. H. Hiortdahl obtained the same product by passing hydrogen sulphide over red-hot cobaltic oxide. The grey, greyish-yellow, or brass-yellow product has a granular fracture. It dissolves in acids, with the evolution of hydrogen sulphide, and presumably hydrogen. It was also prepared by K. Jelinek and J. Zakowsky, and R. Scheuer. V. Caglioti and G. Roberti found that the structure resembles that of bornite, and corresponds with a cubic, face-centred lattice having  $a=9.91$  Å. K. Friedrich examined mixtures of cobalt with up to 33.6 per cent. of sulphur, and the results are summarized in Fig. 118. Cobalt alone separates from alloys rich in cobalt, and the f.p. curve falls to a eutectic at  $879^\circ$  and 26.6 per cent. of sulphur; it then rises to a maximum at  $935^\circ$  and 29.3 per cent. of sulphur, corresponding with the tetratrisulphide. This compound forms solid soln. with up to 72.3 per cent. of cobalt. The form of the curve indicates the existence of a compound  $\text{CoS}$ , but alloys of this composition lose sulphur at ordinary atm. press. At lower temp., there are indications of the formation of a **cobalt hexitapentasulphide**,  $\text{Co}_6\text{S}_5$ —the composition may be  $\text{Co}_5\text{S}_4$ . It was found that the mixtures become porous as the sulphur is increased and the colour passes progressively from cobalt-white to bronze-yellow. Only alloys with over 68.7 per cent. of cobalt are attracted by a magnet.

J. Middleton described a simple **cobaltous sulphide**,  $\text{CoS}$ , or *cobalt sulphide*, as occurring in steel-grey masses at the Khetri mines, Jaipur—also spelt Jeypoor, and Syepoore—Rajputana, India. Hence the mineral was called **jaipurite**—also *jeypoorite*, by W. A. Ross; *syepoorite*, by J. F. L. Hausmann, and J. Nicol; and *Graukobalterz*, by F. von Kobell. According to R. A. Cooper, the so-called mineral *modderite* is jaipurite. The evidence is not conclusive. J. Middleton said that the mineral is used by Indian jewellers for staining gold a delicate rose-colour. The sp. gr. is 5.45. According to F. R. Mallet, only cobaltite and danaite occur in the Jaipur locality, and the cobalt ore from the Khetri mines, sold to the Indian enamellers under the name of *sehta*, produces different shades of blue, not red, enamels on gold and silver. A. Breithaupt also described a mineral resembling linnæite from Reuss, in Rutenia, and hence called it **rutenite**. The compact,

silver-white to bronze-yellow material has a black streak, a hexahedral cleavage, an uneven fracture, sp. gr. 4.923, and hardness 4 to 5. M. Adam supposed that this mineral is the same as jaipurite; C. F. Plattner said that rutenite is a cobalt sulphide with very little nickel, and traces of arsenic.

J. L. Proust, and W. A. Lampadius observed that cobalt and sulphur unite with incandescence, when the mixture is heated. R. Scheuer said that  $475^{\circ}$  is a suitable temp., and if this temp. be exceeded very much, the product will have too small a proportion of sulphur. R. Schenck and E. Raub obtained cobalt sulphide by the action of sulphur dioxide on the metal at  $700^{\circ}$ . The reaction:  $3\text{Co} + \text{SO}_2 = \text{CoS} + 2\text{CoO}$ , is irreversible; they also obtained the sulphide by the action of cobalt sulphate on the metal at about  $300^{\circ}$ :  $\text{CoSO}_4 + 4\text{Co} = \text{CoS} + 4\text{CoO}$ —the vap. press. is about 1 atm. at  $540^{\circ}$ .

A. Baumé obtained the sulphide by heating cobalt with an alkali and calcium sulphate. J. L. Proust also prepared the sulphide by dehydrating the hydrated sulphide, and also by the action of sulphur on cobalt oxide. E. Weinschenk obtained regular crystals of the sulphide by sublimation from a mixture of cobalt oxide, sulphur, and ammonium chloride, and also by heating a mixture of cobalt oxide and ammonium thiocyanate in a sealed tube at  $180^{\circ}$ . R. Scheuer obtained a mixture of sulphides— $\text{CoS}_2$ ,  $\text{Co}_2\text{S}_3$ , and  $\text{CoS}$ —by passing hydrogen sulphide over the oxide at a high temp.—at  $500^{\circ}$ , the disulphide predominates; at  $650^{\circ}$ , the hemitrisulphide; and at  $700^{\circ}$ , the hemitrisulphide and the monosulphide are present in about equal proportions. G. P. Schweder obtained the sulphide by reducing cobalt sulphate with hydrogen, carbon, or carbon monoxide; A. Mourlot, with carbon; and H. Rose, with admixed sulphur in an atm. of hydrogen. T. H. Hiortdahl obtained the sulphide in steel-grey, prismatic crystals by fusing a mixture of anhydrous cobalt sulphate, barium sulphide, and an excess of sodium chloride; and H. Baubigny, by heating a neutral soln. of cobalt sulphate, sat. with hydrogen sulphide, in a sealed tube. A. Carnot added that when hydrogen sulphide is passed over a heated cobalt salt, a mixture of sulphides is formed, not of constant composition. G. Geitner obtained the sulphide by heating cobalt sulphite in a sealed tube at  $200^{\circ}$ .

Solutions of cobalt salts, in the presence of free acid, are not precipitated by hydrogen sulphide, but, in the absence of free acid, **hydrated cobaltous sulphide** is precipitated. The formation of this hydrate by the action of hydrogen sulphide on a soln. of, say, cobalt acetate, by the action of water saturated with hydrogen sulphide on a slurry of cobalt hydroxide or carbonate, and by the action of an alkali sulphide on a soln. of a cobalt salt, was described by J. L. Proust, K. Jellinek and J. Zakowsky, L. L. de Koninck, L. Moser and M. Behr, O. Ruff and B. Hirsch, R. Scheuer, and A. Villiers. F. Strohmeier obtained a precipitate which filters readily by saturating with hydrogen sulphide 100 c.c. of a 0.1*N*-soln. of a cobalt salt, adding 5 c.c. of 5*N*- $\text{NH}_4\text{OH}$ , and passing hydrogen sulphide into the boiling soln. The precipitate is washed with a hot soln. of 0.1*N*- $\text{NH}_4\text{NO}_3$  and 0.05*N*-( $\text{NH}_4$ ) $_2\text{S}$ . According to H. Baubigny, the composition of the product of the action of hydrogen sulphide on neutral and feebly acidic soln. of cobalt salts depends on the concentration of the soln., on the nature of the acid—*vide* 10. 57, 9—on the concentration of the hydrogen sulphide in the soln., and on the time. Cobalt sulphide precipitates more quickly than nickel sulphide from neutral, and very feebly acidic soln., and in more acidic soln., nickel sulphide is precipitated more quickly. The error due to the incompleteness of the precipitation, with increasing acidity of the soln., is illustrated by Fig. 119, due to M. M. Haring and M. Leatherman. G. Bruni and M. Padoa studied the effect of increasing the conc. of the hydrogen sulphide in the soln. by working at press. above atmospheric.

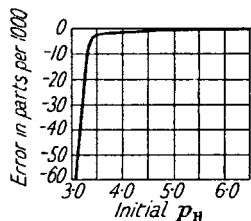


FIG. 119.—The Effect of the Acidity of the Solution on the Precipitation of Cobalt Sulphide.

A. Terreil found that if acetates, citrates, tartrates, and salts of other organic acids be present, cobalt sulphide is precipitated from soln. of cobalt salts by hydrogen sulphide, and this the more rapidly, the less the acidity of the soln. All the cobalt is not precipitated if oxalates are present; and F. Field observed that tartaric or citric acid inhibits the precipitation of cobalt sulphide by hydrogen sulphide. The subject was discussed by F. Uebelhör, H. Vestner, L. L. de Koninck, L. L. de Koninck and M. Ledent, L. Bruner, H. Delffs, G. Chesneau, O. F. Tower, and A. Villiers—*vide* nickel sulphide. U. Dreyer and A. Richter obtained cobaltous sulphide by the action of sodium sulphide on a soln. of potassium cobaltic nitrite. O. W. Gibbs said that when a soln. of a cobaltous salt is treated with a boiling soln. of sodium sulphide, the precipitated sulphide is stable in air, and the precipitate is not soluble in an excess of colourless ammonium or sodium monosulphide, but with higher sulphides, the cobalt sulphide may dissolve—the soln. is stable in air, and it is not decomposed by boiling, or by the addition of sulphuric acid, but the sulphide is precipitated by ammonium chloride. According to W. Herz, cobalt sulphide prepared by precipitation from a soln. of cobalt nitrate, by ammonium sulphide, and washed by decantation with water, is, when freshly-prepared, soluble in dilute, say, 2*N*-hydrochloric acid, with the evolution of hydrogen sulphide. When the precipitate is exposed to air, it is partly converted into cobalt sulphate, and when treated with dil. hydrochloric acid, it partly dissolves without evolving hydrogen sulphide; the remainder of the cobalt sulphide is insoluble, presumably because it has been polymerized or coagulated—*vide* nickel sulphide. S. M. Kusmenko found that with mixtures of cobalt and zinc or manganese sulphates in gelatin, the less soluble sulphide is precipitated first by sodium sulphide. According to G. Chesneau, and R. Scheuer, when a soln. of a cobalt salt is treated with a soln. of an alkali polysulphide, sat. with sulphur, a black **cobalt hemiheptasulphide** is formed, approximating  $\text{Co}_2\text{S}_7$ . The black crystals are said to be insoluble in a soln. of an alkali monosulphide, but soluble in a soln. of sulphur in alkali monosulphide.

A. Terreil, and F. J. Faktor observed that when sodium thiosulphate is added to a rose-red soln. of a cobalt salt, the colour becomes blue, and when the mixture is boiled, some cobalt sulphide is precipitated, and on evaporating the mixture and heating it to 100° or 120°, the conversion to sulphide is complete. O. W. Gibbs, and J. T. Norton observed that cobalt is quantitatively precipitated as sulphide when a cobalt salt is heated with sodium thiosulphate in neutral soln., or in soln. acidified with acetic acid, but not so if a mineral acid is present. O. Brunck found that sodium hyposulphite precipitates the sulphide from soln. of cobalt salts—particularly if the liquid be warm; the presence of ammonia favours the precipitation. R. Schiff and N. Tarugi found that ammonium thioacetate in ammoniacal, but not in acidic, soln. precipitates cobalt sulphide. E. Beutel and A. Kutzelnigg studied the anodic formation of sulphide films.

H. Vestner observed that with 0.001*N*- to 0.0001*N*-soln. of cobalt salts, hydrogen sulphide furnishes a **colloidal solution** of cobalt sulphide; and C. Winssinger prepared a colloidal soln. of cobalt sulphide by working with very dil. soln. and removing the soluble salts by dialysis. The greenish-brown hydrosol can be prepared only in very dil. soln., since it so easily flocculates; and it is readily oxidized by air. The preparation of the hydrosol was also described by A. Lottermoser. A. Müller employed glycerol to prevent the coagulation of the hydrosol, and J. Hausmann recommended gelatin as a protective colloid. The preparation of rhythmic rings by the diffusion of a soln. of sodium sulphide in gelatin associated with a cobalt salt, was discussed by J. Hausmann, S. M. Kusmenko, and O. F. Tower and E. E. Chapman; and F. E. Lloyd and V. Moravek, and E. R. Riegel obtained rhythmic rings in silica gel. P. B. Ganguly and N. R. Dhar studied the coagulation of the colloidal soln. in light.

Precipitated cobalt sulphide is a black powder, but the silver-white crystals prepared by E. Weinschenk have a reddish tinge. According to N. Alsén, W. F. de

Jong and H. W. V. Willems, P. P. Ewald and C. Hermann, and V. M. Goldschmidt, the crystals of the anhydrous sulphide, like millerite, are trigonal, with  $a=3.37$  Å.,  $c=5.14$  Å., and  $a:c=1:1.52$ . V. Caglioti and G. Roberti gave  $a=3.38$  Å.,  $c=5.20$  Å., and  $a:c=1:1.54$ ; the Co-S atoms are 2.33 Å. apart. The subject was discussed by A. Westgren, O. Stelling, and J. W. Gruner. J. Middleton gave 5.45 for the sp. gr. of jaipurite; and A. Breithaupt, 4.923 for the sp. gr. of rutenite. W. F. de Jong and H. W. V. Willems calculated 5.98 for the sp. gr. from the lattice constants. H. V. Regnault obtained 0.12512 for the sp. ht. between 13° and 98°. A. Mourlot found that the sulphur can be nearly all expelled by heating the sulphide in an electric-arc furnace. The m.p. of cobalt sulphide depends on the sulphur-content, and decreases as the proportion of sulphur is reduced, Fig. 117; K. Friedrich gave 1116° for the m.p. of CoS, and W. Biltz said that the m.p. exceeds 1100°. J. Thomsen gave for the heat of formation  $(\text{Co}_2\text{S}, \text{Aq.})=21.71$  Cals., and M. Berthelot, 21.9 Cals.; and J. Thomsen gave for the reaction  $[\text{Co}(\text{OH})_2, \text{H}_2\text{S}_{\text{aq.}}]=17.41$  Cals.; and for  $[\text{Co}(\text{NO}_3)_2, \text{H}_2\text{S}_{\text{aq.}}]=-3.68$  Cals. The subject was discussed by G. Beck, and K. Jellinek and J. Zakowsky. W. Herz studied the entropy, and the vibration frequency. O. C. M. Davis and F. W. Rixon studied the relation between the heat of formation and the colour.

M. Kimura and M. Takewaki observed that cobalt sulphide strongly absorbs ultra-violet rays; A. Mickwitz studied the absorption spectrum; O. Stelling, the X-ray absorption spectrum; O. Rohde, and B. Aulenkamp, the photoelectric properties; and F. Trey, the electrolysis of the compressed powder. W. A. Lampadius, and G. Wiedemann said that cobalt sulphide is feebly ferromagnetic; T. H. Hiortdahl said that it is non-magnetic; and S. Veil observed that the magnetic susceptibility decreases with repeated heating under water at 120° to 210°. W. Klemm and W. Schüth found the mol. magnetic susceptibilities at 20°, 250°, 290°, 365°, and 425° to be, respectively,  $\chi_{\text{mol.}} \times 10^6 = 557, 436, 443, (456),$  and 434 for a field of 2040 gauss.

According to H. Rose, if cobalt sulphide and sulphur be heated in hydrogen, the products obtained vary according to the temp.—cobalt disulphide, hemitrisulphide, and the monosulphide, and at a white-heat, *cobalt hemisulphide*,  $\text{Co}_2\text{S}$ . G. P. Schweder also noted the reduction of the heated sulphide by hydrogen. S. Miyamoto noted that the sulphide is reduced by hydrogen in the silent discharge. G. C. Winkelblech, H. W. F. Wackenroder, R. Scheuer, and W. Herz observed that moist, precipitated sulphide slowly oxidizes when it is exposed to air, with the formation of cobalt sulphate. P. de Clermont and H. Guiot observed that when the moist, freshly-precipitated sulphide is exposed to air, oxidation is not rapid enough to produce a rise of temp. such as occurs with nickel and manganese sulphides. O. W. Gibbs said that the dry sulphide is stable in air at ordinary temp., and oxidizes to sulphate only when it is heated. K. Friedrich observed that when the sulphide is heated in air, sulphur dioxide begins to be evolved at 684°; and in oxygen, at 708°, when the grain-size is 0.1 to 0.2 mm.; with increasing grain-size, the temp. of oxidation is raised. The sulphide does not decrepitate when heated at a low temp. F. Feigl showed that when boiled with animal charcoal in alkaline soln., cobalt sulphide is oxidized to sulphate by the oxygen adsorbed by the charcoal. A. Maifert found that ozone converts the sulphide first into sulphate, and then into sulphuric acid and cobalt peroxide.

T. H. Hiortdahl observed that water slowly transforms cobalt sulphide into the sulphate. H. V. Regnault, and F. Foreman found that at a red-heat, water vapour attacks the sulphide moderately; and J. A. McLarty, that with water vapour under press., cobalt oxide and hydrogen sulphide are formed. According to O. Weigel, water dissolves  $41.62 \times 10^{-6}$  mol of cobalt sulphide per litre, or 0.000379 per cent. L. Moser and M. Behr gave  $10^{-9.28}$  mol per litre for the solubility in water, and  $1.9 \times 10^{-27}$  for the solubility product. A. Mickwitz calculated for the solubility,  $0.3 \times 10^{-5}$  to  $1.0 \times 10^{-5}$  per cent. metal cobalt. Observations were also made by L. Bruner and J. Zawadzky, and I. M. Kolthoff. J. L. R. Morgan

and A. H. Gotthalf found the relative solubility products of some sulphides, in mols per litre, in the presence of the  $S''$ - and  $HS'$ -ions, contained in 0.1*N*- $K_2S$ , to be Ni, 0.0191; Co, 0.0034; Cu, 0.00021; and Pb, 0.00024. A. Mickwitz found that in dil. soln., with  $Na_2S$  as precipitating agent, sat. soln. contain  $0.3 \times 10^{-5}$  per cent. of Co, and the precipitate is **cobalt hydroxyhydrosulphide**,  $Co(OH)(HS)$ , and when an excess of hydrogen sulphide is used as precipitant, there is evidence of the formation of **cobalt hydrosulphide**,  $Co(SH)_2$ . According to J. A. Arfvedson, if hydrogen be passed over red-hot cobalt sulphate, sulphur dioxide and water are evolved, and what was thought to be **cobalt oxysulphide**,  $Co_2OS$ , or  $CoO.CoS$ , is formed. When heated in air to redness, this product forms sulphur dioxide and cobaltic oxide; and with cold hydrochloric acid, cobalt oxide passes into soln., and cobalt sulphide remains; with the hot acid, some cobalt sulphide is also dissolved.

H. Rose found that cobalt sulphide is not attacked by chlorine in the cold, and the attack is slow when the sulphide is heated. E. Zielinsky studied the chloridizing of the sulphide. H. W. F. Wackenroder said that the precipitated sulphide dissolves in mineral acids when tolerably concentrated, but is very sparingly soluble in cold, dil. acids. E. Weinschenk observed that crystalline cobalt sulphide is attacked very slowly by conc. hydrochloric acid; and O. W. Gibbs, and L. L. de Koninck said that the sulphide is insoluble in dil. hydrochloric acid, but T. H. Hiortdahl said that it is soluble. Although cobalt and nickel sulphides are virtually insoluble in cold, dil. hydrochloric acid, neither is precipitated in the presence of that reagent by hydrogen sulphide; consequently, the sulphide probably changes into a less soluble form as soon as it has been precipitated—*vide* nickel sulphide. L. Moser and M. Behr found that freshly-precipitated, moist cobalt sulphide dissolves in hot or cold 0.5*N*-HCl, with the evolution of hydrogen sulphide; and air-dried cobalt sulphide dissolves partially in hydrochloric acid without giving off hydrogen sulphide. The air-dried sulphide is thus supposed to consist of sulphate mixed with insoluble, or polymerized sulphide. W. Herz noted that the precipitated sulphide becomes insoluble in 2*N*-HCl, as it is allowed to age. A. S. Komarowsky observed that the presence of a few drops of a 3 per cent. soln. of hydrogen dioxide makes cobalt sulphide dissolve very easily in 0.5*N*-soln. of mineral acids. P. Berthier observed that the moist sulphide dissolves in sulphurous acid; and J. Milbauer and J. Tucek, that the sulphide is oxidized by sulphur dioxide to form sulphate:

	500°	600°	700°	800°
Cobalt sulphate .	44.08	17.29	10.18	6.97 per cent.
Cobalt oxide .	—	53.75	71.29	91.93 „

H. Danneel and F. Schlottmann found that cobalt sulphide resists attack by sulphuryl chloride at ordinary temp., and at 300° to 350°, 5 to 9 per cent. is decomposed in one hour. L. Moser and M. Behr found that at 20°, a 2*N*-soln. of sulphuric acid, saturated with hydrogen sulphide, dissolves  $1.72 \times 10^{-4}$  mol of the cobalt sulphide per litre. V. Stanek observed that when the freshly-precipitated sulphide is heated with colourless ammonium sulphide in a sealed tube, at 200°, for 8 hrs., it suffers no perceptible change; but R. Popper found that cobalt sulphide is completely soluble in a soln. of ammonium polysulphide. P. de Clermont, and P. de Clermont and J. Frommel found that the sulphide is slowly decomposed by a boiling soln. of ammonium chloride.

G. P. Schweder observed that the sulphide is desulphurized when heated with carbon; and A. Mourlot noted the same thing in an electric furnace. F. Feigl found that the sulphide is oxidized to sulphate when boiled with water and bone charcoal. According to T. H. Hiortdahl, cobalt sulphide dissolves very slowly in acetic acid, but H. W. F. Wackenroder, and L. L. de Koninck said that the sulphide is scarcely soluble in dil. acetic acid. A. S. Komarowsky observed that in the presence of a little 3 per cent. soln. of hydrogen dioxide, the dissolution of the sulphide

in acetic acid proceeds very quickly. F. Field observed that the sulphide is slightly soluble in tartaric and citric acids. L. L. de Koninck said that the sulphide is not soluble in a cold soln. of potassium cyanide; and A. Guyard added that the freshly-precipitated sulphide is soluble in not very dil. soln. of potassium cyanide, and in this respect it differs from nickel sulphide—J. Haidlen and R. Fresenius said that a brownish-yellow soln. of a complex cyanide is formed. A. Guyard found that a hot soln. of alkali thiocyanate slowly dissolves the sulphide. B. L. Moldavsky and Z. I. Kumari studied the catalytic effect of the sulphide on the hydrogenation of thiophene.

N. Parravano and P. Agostini observed that aluminium, in the thermite process, reduces the sulphide to metal. J. B. Cammerer observed that a soln. of ferric chloride slowly transforms the sulphide into cobaltous chloride. E. Schürmann found that cobalt sulphide in contact with soln. of copper sulphate or lead nitrate is completely converted; partially decomposed in contact with soln. of zinc, nickel, or ferrous sulphate; and not decomposed by a soln. of manganese sulphate. E. F. Anthon observed that precipitated cobalt sulphide precipitates sulphides from aq. soln. of cadmium sulphate, lead acetate, ferric chloride, nickel nitrate, copper sulphate, and silver nitrate. C. Palmer and E. S. Bastin found that cobalt sulphide precipitates silver from a soln. of silver nitrate. According to R. Schenck and E. Raub, nickel reacts rapidly with sulphur dioxide at  $550^{\circ}$ , but equilibrium is established only after many days, complete conversion into nickel oxide and monosulphide being effected. The equilibrium is univariant, as there are three solid phases, but by removing part of the sulphur dioxide, one of these disappears and the equilibrium becomes bivariant. The three phases appear to be nickel oxide, nickel sulphide, and the  $\gamma$  solid solution; with low pressures of sulphur dioxide, the nickel sulphide phase disappears. The reverse reaction, with the formation of nickel from nickel oxide and sulphide, proceeds only as far as the solid solution phase below the m.p., at about  $1400^{\circ}$ ; bundles of fine, hair crystals of this phase, or possibly of  $\text{Ni}_3\text{S}_2$ , can be seen throughout the reacting mass in the early stages of this reaction.

H. de Sénarmont, and R. Scheuer prepared **cobaltosic sulphide**,  $\text{Co}_3\text{S}_4$ , as a dark grey powder, by heating a soln. of cobalt chloride and ammonium polysulphide in a sealed tube at  $160^{\circ}$ . I. and L. Bellucci obtained it by keeping a mixture of cobalt carbonate, potassium carbonate and sulphur at a white-heat for a long time. W. F. de Jong and H. W. V. Willems obtained it by heating precipitated cobalt sulphide for 10 hrs. at  $400^{\circ}$  to  $450^{\circ}$  in a current of hydrogen sulphide. The X-radiogram coincides with that of linnæite, and it has a face-centred, cubic lattice  $a=9.36$  Å., 8 mols. per unit cell; and a calculated sp. gr. of 4.86. The X-radiograms of G. Menzer indicate that the three minerals, linnæite,  $\text{Co}_3\text{S}_4$ , polydymite,  $\text{Ni}_3\text{S}_4$ , and sychnodymite,  $(\text{Co,Cu,Ni})_3\text{S}_4$ , are structurally the same; and M. N. Short and E. V. Shannon concluded that there are ternary and binary series of isomorphous mixtures in which the terminal members are ideal polydymite, ideal linnæite, and the unknown sulphomagnetite,  $\text{Fe}_3\text{S}_4$ —*vide infra*. H. de Sénarmont found that cobaltosic sulphide is not attacked by dry air; and J. Joly noted that sulphur begins to be evolved near  $480^{\circ}$ . J. Lemberg found that a boiling sulphuric acid soln. of silver sulphate colours a section blue in about 5 mins.; and bromine in alkaline soln. produces a dark film in 15 mins. M. Leo observed that in a soln. of a salt of gold, a film of gold is deposited on the sulphide; and with a soln. of potassium bromate, it is blackened. E. F. Smith found that the sulphide is completely decomposed by sulphur monochloride in a sealed tube at  $170^{\circ}$ .

J. J. Berzelius, and L. R. von Fellenberg prepared **cobaltic sulphide**,  $\text{Co}_2\text{S}_3$ , or **cobalt sesquisulphide**, by heating cobalt oxide strongly with sulphur and potassium hydroxide or carbonate, and washing the cold product—R. Schneider added that the cobaltic sulphide so obtained is impure. The sulphide is obtained by heating to bright redness, cobalt chloride with 12 times its weight of a mixture of equal parts of sodium carbonate, and sulphur. J. J. Berzelius obtained it by

heating cobaltic oxide not quite to redness in a current of hydrogen sulphide and J. A. Arfvedson, by passing hydrogen sulphide over red-hot cobalt oxysulphide. T. H. Hiortdahl, and R. Scheuer obtained cobaltic sulphide by heating a mixture of cobalt and sulphur preferably between  $350^{\circ}$  and  $400^{\circ}$ ; or by the action of hydrogen sulphide on cobaltic oxide between  $600^{\circ}$  and  $650^{\circ}$ —some cobalt monosulphide and disulphide are formed at the same time. R. Scheuer observed that yellow ammonium sulphide precipitates cobalt disulphide, along with a little cobaltic sulphide, from a cold soln. of a cobaltous salt; and when the mixture is boiled, with exclusion of air, cobaltic sulphide is formed in excess. E. M. Dingler observed that when an ammoniacal soln. of a cobalt salt is oxidized by air, and then treated with a yellow soln. of ammonium sulphide, hydrated cobaltic sulphide is precipitated; and the same product is obtained when a cobaltic hexammine or pentammine salt is similarly treated. Cobaltic sulphide appears in iron-grey, tabular crystals. F. W. Clarke reported that the sp. gr. is 4.8. I. and L. Bellucci said that cobaltic sulphide is non-magnetic, and when heated, gives off sulphur. It is not decomposed by water or by alkali-lye. L. R. von Fellenberg observed that when heated in chlorine, it is decomposed, forming sulphur and cobalt chlorides. R. Schneider found that it is slowly attacked by cold hydrochloric acid and aqua regia, and when boiled, sulphur separates out. According to H. Fleck, the hydrated cobaltic sulphide is not soluble in a soln. of potassium cyanide—*vide infra*, horbachite.

According to J. J. Setterberg, **cobalt disulphide**,  $\text{CoS}_2$ , can be prepared by rapidly igniting the recently-precipitated carbonate, and heating to a little below redness a mixture of the product with 3 times its weight of sulphur—if the product is not black, it is again mixed with sulphur and ignited. L. Playfair and J. P. Joule used a similar process. I. and L. Bellucci obtained, not the disulphide, but only cobaltic sulphide by this process, and by keeping the temp. at a white-heat for a long period. Cobaltous sulphide is also obtained by passing hydrogen sulphide over cobaltic oxide at a temp. much below redness and boiling the dark grey mass with hydrochloric acid. R. Scheuer employed a temp. between  $250^{\circ}$  and  $600^{\circ}$ , and obtained the disulphide mixed with cobaltic and cobaltous sulphides. He also obtained it by heating a mixture of cobalt and sulphur to  $175^{\circ}$  to  $225^{\circ}$ . Yellow ammonium sulphide also produces this sulphide mixed with cobaltic sulphide when it is added to a hot or a cold soln. of a cobaltous salt. W. F. de Jong and H. W. V. Willems obtained the disulphide by heating powdered cobalt sulphide with sulphur at  $160^{\circ}$  for 30 to 40 hrs., and washing out the free sulphur with carbon disulphide. K. Johansson described cobaltiferous pyrite—**cobalt pyrite**,  $(\text{Co}, \text{Fe})\text{S}_2$ , of sp. gr. 4.965, and hardness 6.

The X-radiogram showed that the crystals are cubic, and of the pyrite type, with the parameter  $a=5.64 \text{ \AA}$ ., the Co-S atoms are  $2.38 \text{ \AA}$ . apart. The lattice structure was also discussed by J. W. Gruner, V. M. Goldschmidt, P. Niggli, and P. P. Ewald and C. Hermann. According to W. F. de Jong and H. W. V. Willems, the calculated sp. gr. is 4.55. According to L. Playfair and J. P. Joule, the sp. gr. is 4.269. J. J. Setterberg, and R. Scheuer found that the dull black powder gives off sulphur at a red-heat to form the grey monosulphide; it is not attacked by boiling alkali, or by acids, with the exception of nitric acid and aqua regia. The product obtained by the second process is oxidized to sulphuric acid and cobaltous sulphate when exposed, in a moist state, to air.

R. Schneider<sup>2</sup> melted cobalt, or a cobalt salt, with potassium carbonate and sulphur, and, on washing the cold product with water, obtained greyish-white, hexagonal plates mixed with a black, crystalline powder, but he was unable to separate the two. J. Milbauer melted cobalt oxide with five times its weight of potassium thiocyanate for half an hour at a red-heat, and washed the product with water. The dark grey mass had a metallic lustre, and under the microscope showed a crystalline structure. The analysis corresponded with **potassium cobalt decasulphide**,  $\text{K}_2\text{Co}_{11}\text{S}_{10}$ . It dissolves slowly in hydrochloric acid, and in aqua

regia in the cold; rapidly when heated. Hydrofluoric and sulphuric acids dissolve it only when warm. A soln. of ammonium sulphide, even when hot, has no action; organic acids, 12 per cent. hydrochloric acid, alkali-lye, and soln. of potassium cyanide, copper sulphate, and silver nitrate are without action. H. Brunner reported **sodium cobalt disulphide**,  $\text{Na}_2\text{CoS}_2$ , to be formed as a yellow, crystalline mass, by heating cobalt oxalate with sodium thiosulphate. The product is easily oxidized in air. F. J. Faktor heated a mixture of anhydrous cobalt chloride and anhydrous sodium thiosulphate, and obtained a green mass which, when washed with water and alcohol, furnished **sodium cobalt pentasulphide**,  $\text{Na}_2\text{Co}_4\text{S}_5$ , as a black powder. I. and L. Bellucci obtained only cobalt sesquisulphide when mixtures of a cobalt salt, alkali hydroxide, and sulphur are fused at a high temp. A similar product was obtained in the corresponding attempt to prepare **barium cobalt sulphide**.

W. L. Faber described a mineral from the Patapsco mine in Carroll Co., Maryland, and he called it **carrollite**. Analyses by W. L. Faber, J. L. Smith and G. J. Brush, E. V. Shannon, W. F. de Jong and A. Hoog, and F. A. Genth correspond with **copper sulphocobaltite**,  $\text{CuS} \cdot \text{Co}_2\text{S}_3$ , or  $\text{Cu}(\text{CoS}_2)_2$ ; it can also be regarded as a member of the group of **sulphomagnetites**,  $\text{R}_3\text{S}_4$ , which includes *polydymite*, *linnæite*, and *synchodymite*—vide nickel sulphides. The mineral occurs in octahedral crystals belonging to the cubic system, and it also occurs massive. Its colour is light steel-grey, with a faint reddish tint. Its fracture is uneven, approaching conchoidal, and the lustre is metallic. W. F. de Jong and A. Hoog observed that the X-radiograms are very similar to those of polydymite, and linnæite. The face-centred, cubic lattice has eight  $\text{R}_3\text{S}_4$ -, or  $\text{CuCo}_2\text{S}$ -molecules per unit cell; and the parameter  $a=9.458 \text{ \AA}$ . The sp. gr. is 4.85; and the hardness, 5.5.

W. Guertler and H. Schack found that lead and cobalt and their sulphides are incompletely miscible when molten; and in the system:  $\text{Pb}-\text{Co}-\text{PbS}-\text{CoS}$ , they observed the solid phases:  $\text{Pb}+\text{Co}+\text{Co}_5\text{S}_4$ ;  $\text{Pb}+\text{PbS}+\text{Co}_5\text{S}_4$ ; and  $\text{Co}_5\text{S}_4+\text{CoS}+\text{PbS}$ . M. Houdard heated a mixture of aluminium and cobalt in a current of hydrogen sulphide, and obtained golden-yellow spangles, which rapidly blackened. No definite **aluminium cobalt sulphide** was formed. F. Feigl reported **stannic cobalt sulphide** to be formed when a mixed soln. of stannic and cobalt salts is heated with hydrogen sulphide. W. Guertler, and W. Guertler and H. Schack made a study of a part of the ternary system:  $\text{Pb}-\text{Co}-\text{S}$ , but did not observe the formation of **lead cobalt sulphide**.

In 1746, G. Brandt<sup>3</sup> found a ferruginous cobalt sulphide—"cobalt with iron and sulphuric acid"—at Bastnaes, near Riddarhyttan, Sweden; A. Cronsted called it *cobaltum ferro sulphurato mineralisatam*; C. Linnæus, *cobalt pyriticosum*; and B. G. Sage, and J. B. L. Romé de l'Isle, *mine de cobalt sulfureuse*, after W. Hisinger's analysis, which showed the mineral to be a cobalt sulphide. J. F. L. Hausmann called it *cobalt pyrites*; C. F. Rammelsberg called it *cobalt-nickel pyrites*; F. S. Beudant, *koboldin*; and W. Haidinger, *linnæite*, after Linnæus. J. D. Dana described a nickeliferous variety from Siegen, Prussia, and called it *siegenite*—vide *infra*; and one from Müsen, Prussia, he called *musenite*.

The occurrences of linnæite in Westphalia and the Rhine provinces were described by A. Breithaupt, C. Heusler, R. Hundt, H. Laspèyres, F. Roth, R. Scheibe, C. Schnabel, M. Schulze, and J. C. Ullmann; in Saxony, by A. Frenzel; in Siberia, by M. Websky; in Moravia, by F. A. Kolenati, and F. Kretschmer; in Great Britain, by A. Terrell and A. des Cloizeaux; in Sweden, by W. Hisinger, G. Leonhard, A. Erdmann, and J. J. Berzelius; at Katanga, Belgium Congo, by H. Buttgenbach; in the United States—Maryland and Missouri—by F. A. Genth.

Analyses were reported by T. Haeger, F. C. Wernekinck, W. Witteborg, C. F. Rammelsberg, P. T. Cleve, G. Wolf, M. Legraye, and F. A. Genth. M. L. Frankenheim, and L. S. Randall gave the formula,  $\text{CoS} \cdot \text{Co}_2\text{S}_3$ , or  $\text{Co}_3\text{S}_4$ ; C. F. Rammelsberg gave  $2\text{RS} \cdot \text{RS}_2$ , and later,  $\text{R}_2\text{S}_{11}$ , or  $2\text{RS} \cdot 3\text{R}_2\text{S}_3$ ; P. Groth, and A. Schoep,  $(\text{Ni}, \text{Co}, \text{Fe})(\text{Ni}, \text{Co}, \text{Fe})\text{S}_2\text{CoS}_2$ , or  $(\text{Co}, \text{Ni})_3\text{S}_4$ ; H. F. Collins,  $(\text{Ni}, \text{Cu}, \text{Fe}, \text{Co})\text{S} \cdot \text{CoS}_2$ ;



W. Stahl,  $(\text{Ni}, \text{Co}, \text{Cu}, \text{Fe})_4\text{S}_5$ ; and A. Eichler and co-workers,  $5\text{Co}_3\text{S}_4 \cdot 6\text{NiS}_4$ . The mineral linnæite was considered by M. N. Short and E. V. Shannon to be one of the terminal members,  $\text{Co}_3\text{S}_4$ , of the ternary isomorphous series,  $(\text{Co}, \text{Ni}, \text{Fe})_3\text{S}_4$ , just as polydymite,  $\text{Ni}_3\text{S}_4$ , is taken to be a second end-member, and  $\text{Fe}_3\text{S}_4$ , a third end-member. The formula,  $\text{CoS} \cdot \text{Co}_2\text{S}_3$ , or  $\text{Co}(\text{CoS}_2)_2$ , makes linnæite analogous with the spinels, or a member of the *sulpho-spinels*.

Linnaite occurs in granular or compact masses as well as in octahedral crystals belonging to the cubic system. The fracture is uneven and almost conchoidal. The colour is pale steel-grey, or cream with a tinge of yellow, and it tarnishes to a yellowish-red, or to copper-red; the streak is blackish-grey; and the lustre is metallic. The cubic cleavage is imperfect. Twinning sometimes occurs about the (111)-plane, as in the spinels. F. Becke found that the corrosion figures are analogous to those of magnetite. The subject was also discussed by H. Baumhauer. The crystals were examined by C. Klein, J. C. Ullmann, M. Schulze, R. Scheibe, H. Laspèyres, R. Novacek, A. Terreil and A. des Cloizeaux, P. T. Cleve, and F. A. Genth. G. Menzer examined the X-radiograms of polydymite, linnæite, and sychmodymite, and found them almost identical. The face-centred, cubic lattice has the parameter  $a=9.398 \text{ \AA}$ .; and there are eight  $\text{Co}_3\text{S}_4$ -molecules in the elementary cell. W. F. de Jong found  $a=9.26 \text{ \AA}$ . for linnæite from Littfeld;  $9.42 \text{ \AA}$ ., for that from Müsen. An artificial preparation, obtained by heating cobaltous sulphide in hydrogen sulphide at  $400^\circ$  to  $450^\circ$  for 10 hrs., was very like natural linnæite. G. Natta and L. Passerini found that the cubic lattice of  $\text{Co}_3\text{S}_4$  and of  $\text{Ni}_3\text{S}_4$  is of the spinel type, with  $a=9.41 \text{ \AA}$ . C. F. Rammelsberg gave 4.8 for the sp. gr.; P. T. Cleve, 4.755, and 4.825; C. Schnabel, 5.00; A. Eichler and co-workers, 4.85; H. Buttgenbach, 4.82; and I. I. Saslawsky, 4.808 to 4.816. The last-named also studied the mol. vol. W. F. de Jong calculated a sp. gr. 4.86 from the lattice data. The hardness is 5 to 6. H. Fizeau gave for the coeff. of thermal expansion  $\alpha=0.041037$  at  $40^\circ$ . J. Joly gave  $480^\circ$  for the m.p. F. Beijerinck found that the linnæite is a good electrical conductor; and T. W. Case showed that an exposure of the mineral to light does not perceptibly affect its electrical resistance. E. T. Wherry found linnæite to be a fair radio-detector. J. Lemberg observed that an alkaline soln. of bromine attacks the mineral and produces a surface film of metal peroxide. E. F. Smith observed that the mineral is broken down by sulphur monochloride at  $170^\circ$ . Linnaite dissolves in nitric acid, with the separation of sulphur. J. Lemberg found linnæite is not readily coloured by a soln. of silver sulphate, but a blue coloration appears after a prolonged action at  $100^\circ$ .

The proportion of nickel in the linnæite of the Mine la Motte, Madison Co., exceeds that of the cobalt, and in that case M. N. Short and E. V. Shannon prefer the term **siegenite**, indicated above. The analysis agrees with  $(\text{Fe}, \text{Co}, \text{Ni})_3\text{S}_4$ ; the mineral is isotropic; it has a cream colour with a tinge of yellow; no cleavage pits have been observed; with nitric acid a polished surface acquires a brown stain, and there is some effervescence; mercuric chloride gives indication of producing a brown stain in places; and negative results were obtained with hydrochloric acid, soln. of potassium cyanide and ferric chloride, and with potash-lye. These properties all resemble those of polydymite and of linnæite, but differ from violarite in the absence of a perfect cubic cleavage, and in the colour.

A. Knop<sup>4</sup> described a mineral occurring with the chalcopyrite in the gneiss at Horbach, near St. Blasien, in the Black Forest. It was called **horbachite**. Analyses were reported by A. Knop, and E. Weinschenk. C. F. Rammelsberg represented the composition by the formula:  $15\text{Fe}_2\text{S}_3 \cdot 4\text{NiS}_3$ ; and P. Groth and K. Mieleitner, by  $\text{Fe}_8\text{Ni}_2\text{S}_{15}$ , or  $(\text{Fe}, \text{Ni})_2\text{S}_3$ . E. Weinschenk regarded horbachite as a mixture of iron and nickel monosulphides,  $(\text{Fe}, \text{Ni})\text{S}$ , when  $\text{Fe} : \text{Ni} = 3 : 1$  or  $4 : 1$ . The origin of the mineral was discussed by W. Sauer, and E. Beyschlag and co-workers. The colour of horbachite is dark bronze-brown or steel-grey. The streak is black. It occurs in crystalline masses, with an imperfect cleavage. The sp. gr. is 4.43; and the hardness, 4.5. F. Beijerinck said that the mineral

is a very good electrical conductor. The mineral readily decomposes under the influence of water and moisture, forming sulphates of iron and nickel.

W. Guertler<sup>5</sup> discussed the nickel-cobalt sulphides. W. Guertler and H. Schack observed that cobalt pentitattetrasulphide,  $\text{Co}_5\text{S}_4$ , and nickel tritadisulphide,  $\text{Ni}_3\text{S}_2$ , form a continuous series of solid soln. above  $475^\circ$ ; below this temp., the mass is completely decomposed, with the separation of two new solid soln.

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### § 23. Cobaltous Sulphate

F. A. C. Gren,<sup>1</sup> and W. A. Lampadius obtained a soln. of **cobaltous sulphate**, or simply **cobalt sulphate**,  $\text{CoSO}_4$ , by dissolving the metal or the oxide in dil. sulphuric acid. An aq. soln. of cobaltous sulphate is obtained by dissolving the oxide, hydroxide, or carbonate in dil. sulphuric acid; and on evaporating the liquid at ordinary temp., the *heptahydrate*,  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ , crystallizes out—I. Koppel and H. Wetzel said that the heptahydrate crystallizes from the soln. below  $40\cdot7^\circ$ , and C. D. Carpenter and E. R. Jette, below  $45\cdot1^\circ$ .

Anhydrous cobaltous sulphate was prepared by E. Rothoff, and J. L. Proust by the dehydration of the hydrated salt at a dull red-heat; T. E. Thorpe and J. I. Watts recommended maintaining the hydrate at  $250^\circ$  until all the combined water has been expelled; and the Kali Forschungsanstalt observed it by heating a sat. soln. in an autoclave at  $200^\circ$ . The anhydrous salt was prepared by A. Étard, by boiling a soln. of the hydrated salt in conc. sulphuric acid; A. W. Davidson, by adding a little conc. sulphuric acid to an acetic acid soln. of cobalt nitrate; and by P. Klobb, by adding the hydrated salt to molten ammonium sulphate, and heating the mixture, protected from reducing gases, until the ammonium salt is all volatilized. C. Lepierre and M. Lachaud employed a similar process, and observed that when ammonium hydrosulphate is employed, instead of the normal salt, the cobalt sulphate furnishes fusiform, prismatic, hexagonal crystals, whereas with the normal salt, canary-yellow, octahedral crystals are formed. The difference is due to the presence of about 0.5 per cent. of free sulphuric acid in the fusiform crystals. A. Chatillon, H. P. Corson, R. Romer, T. Thomas, and R. Hocart and A. Serres prepared crystals of the salt; and F. Feigl and H. J. Kapulitzas obtained it from nickel-free oxide.

The heptahydrate occurs rarely as a mineral. The mineral was called *cobalt vitriol* by M. le Blanc, B. G. Sage, J. H. Kopp, and C. C. von Leonhard. It was also called *red vitriol*. F. S. Beudant proposed the name *rhodalose*—from  $\rho\acute{o}\delta\acute{o}\epsilon\iota\varsigma$ , rose-coloured, and  $\alpha\lambda\varsigma$ , salt—but this gave way to W. Haidinger's term *bieberite*, after the longest-known locality, Bieber, in Hesse, where it occurs in the rubbish of some old mines. C. F. Rammelsberg mentioned its occurrence in some mines at Siegen; F. Sandberger, at Alpirsbach; J. F. Vogl, at Joachimstal, Bohemia; A. Lacroix, at Chalanches, Dept. Isère, France; and W. J. Taylor, at Tres Puntas, Copiapo, Chili. C. M. Kersten noted the occurrence of the heptahydrate on specimens of cobalt speiss kept in museums. Analyses of bieberite were reported

by G. C. Winkelblech, C. F. Rammelsberg, F. S. Beudant, and J. H. Kopp; and of the heptahydrate, by J. L. Proust, E. Mitscherlich, and C. F. Bucholz.

I. Koppel and H. Wetzel found that, with sat., aq. soln., the heptahydrate is the solid phase up to 40°, and he estimated that the transition from the heptahydrate to the *hexahydrate*,  $\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$ , occurs at about 40·7°, because J. C. G. de Marignac observed that the hexahydrate separates from the aq. soln. between 40° and 50°. The transition temp. is lowered in the presence of sodium sulphate. C. D. Carpenter and E. R. Jette gave 45·1° for the transition temp. E. Mitscherlich, W. Müller-Erzbach, and T. E. Thorpe and J. I. Watts said that the hexahydrate is obtained by crystallization from an aq. soln. of cobalt sulphate between 20° and 30°. R. Rhomer also prepared the hexahydrate. W. Müller-Erzbach said that the hexahydrate can be obtained by drying the heptahydrate over sulphuric acid; and L. de Boisbaudran also obtained the hexahydrate by carefully warming the heptahydrate, or by contact of the heptahydrate with a fragment of the hexahydrate—*vide infra*, the thermal decomposition of the sulphate. L. Playfair and J. P. Joule, G. N. Wyrouboff, T. E. Thorpe and J. I. Watts, and E. S. Larsen and M. L. Glenn reported the *pentahydrate*,  $\text{CoSO}_4 \cdot 5\text{H}_2\text{O}$ , by drying the heptahydrate or the hexahydrate over sulphuric acid. T. E. Thorpe and J. I. Watts obtained the *tetrahydrate*,  $\text{CoSO}_4 \cdot 4\text{H}_2\text{O}$ , by drying the powdered heptahydrate to a constant weight over sulphuric acid; H. O. Hofman and W. Wanjukoff, by passing a current of dry air over the heptahydrate; A. Fröhde, by adding conc. sulphuric acid to a conc. soln. of cobalt sulphate; and G. Vortmann, by heating cobaltic chloropentamminochloride with a little water and conc. sulphuric acid until all is dissolved, and then heating the mixture on a sand-bath at 220°. When, on cooling, the tetrahydrate separates out, the sulphuric acid is poured away from the crystalline powder, which is washed with cold water and alcohol, and dried on a porous tile. R. Rohmer prepared the tetrahydrate. G. Vortmann reported the possible existence of a *trihydrate*,  $\text{CoSO}_4 \cdot 3\text{H}_2\text{O}$ ; and T. E. Thorpe and J. I. Watts, and L. Playfair and J. P. Joule said that the *dihydrate*,  $\text{CoSO}_4 \cdot 2\text{H}_2\text{O}$ , is formed by boiling the powdered heptahydrate with absolute alcohol; and M. A. Rakuzin and D. A. Brodsky, by allowing the higher hydrate to stand for some time over sulphuric acid. R. Rohmer also prepared the dihydrate. According to A. and H. Benrath, the solid phase in the aq. soln. at 97° is the *monohydrate*,  $\text{CoSO}_4 \cdot \text{H}_2\text{O}$ , which E. Wouff, H. Lescœur, and A. Étard prepared by mixing a conc. soln. of cobalt sulphate with cold, conc. sulphuric acid. R. Rohmer also prepared the monohydrate. T. E. Thorpe and J. I. Watts obtained the monohydrate by heating the heptahydrate to 100°; M. A. Rakuzin and D. A. Brodsky, by heating the heptahydrate 3 hrs. at 98°; F. Krafft, and A. Adolphi, by confining a higher hydrate in vacuo over phosphorus pentoxide; H. O. Hofman and W. Wanjukoff, by passing dry air over the heptahydrate at 58°; E. S. Larsen and M. L. Glenn, by drying the hexahydrate in a desiccator; G. Vortmann, from the mother-liquor after the preparation of the tetrahydrate; W. Ipatéeff and B. Zrjagin, by heating 1·5*N*- or 2*N*- $\text{CoSO}_4$  in a hydrogen or nitrogen atm. under press. at 150°, but J. H. Weibel added that in hydrogen or carbon monoxide, there is no separation at 150°, metal and oxide are precipitated at 250°, and metal only at 300°. The evidence of the chemical individuality of many of those hydrates is not very convincing. A. P. Rostkowsky's vap. press. curves show that only the hepta-, hexa-, and monohydrates are formed as chemical individuals. R. Reinicke studied the hydrates.

P. Klobb said that the **crystals** of the anhydrous salt are amaranth-red octahedra belonging to the cubic system. A. Étard, and C. Lepierre and M. Lachaud reported what they considered to be dimorphous forms—hexagonal and cubic—*vide supra*. R. Hocart and A. Serres found that the crystals of the salt dehydrated at 400° and 700° in ammonium hydrosulphate, are rhombic, with a space-lattice having  $a=4\cdot65$  Å.,  $b=0\cdot71$  Å., and  $c=8\cdot45$  Å., and 4 mols. per unit cell. The dimensions of the lattices of the specimens are the same, but the structures and magnetic

properties are different. The carmine-red crystals of the heptahydrate were found by H. J. Brooke to be monoclinic with the axial ratios  $a:b:c$  1.1835:1:1.4973, and  $\beta=104^\circ 55'$ ; and J. C. G. de Marignac gave 1.1815:1:1.5325, and  $\beta=104^\circ 40'$ . Observations were made by E. Mitscherlich. A. Rosenstiehl observed that the crystals of the heptahydrate are isomorphous with the corresponding heptahydrated zinc, manganese, iron, and nickel sulphates, and the subject was discussed by A. Arzruni, C. F. Rammelsberg, and E. S. von Fedoroff. J. M. Thomson noted the seeding of supersaturated soln. of magnesium sulphate with crystals of heptahydrated cobalt sulphate. E. S. Larsen and M. L. Glenn found the optic axial angle,  $2V$ , of the monoclinic tablets is near  $90^\circ$ ; M. W. Porter gave for  $2V=88^\circ 1'$ , and he noted cleavages on the (001)- and the (110)-faces. H. G. K. Westenbrink examined the X-radiogram and calculated for the cell parameters  $a=15.45$  A.,  $b=13.08$  A., and  $c=20.04$  A., and there are 4 mols. per unit cell. The red crystals of the hexahydrate were found by J. C. G. de Marignac to be monoclinic prisms with the axial ratios  $a:b:c=1.3957:1:1.6976$ , and  $\beta=98^\circ 41'$ . The crystals are isomorphous with the corresponding salts of magnesium and zinc. G. N. Wyruboff gave for the optic axial angle  $2H_a=8^\circ$ , and reported a possible dimorphous form. G. Roasio discussed the orientation of the crystals grown in a magnetic field. E. S. Larsen and M. L. Glenn found that the crystals of the pentahydrate are triclinic with a medium optic axial angle,  $2V$ . A. Fröhde said that the tetrahydrate furnishes a crystalline powder of a peach-blossom colour, and a similar remark was made by G. Woulf about the monohydrate; E. S. Larsen and M. L. Glenn obtained the monohydrate in fibres and crusts by evaporating an aq. soln. of the salt to dryness, whereas that obtained by the dehydration of the hexahydrate in a desiccator furnishes crystals with an optic axial angle having  $2V$  nearly  $90^\circ$ .

According to L. Playfair and J. P. Joule, the **specific gravity** of the anhydrous sulphate is 3.531; O. Pettersson gave 3.614, 3.615 at  $15.6^\circ$  to  $16^\circ$ ; L. Playfair, 3.444; T. E. Thorpe and J. I. Watts, 3.472 at  $157^\circ$ ; and C. Lepierre and M. Lachaud, 3.65 for the octahedral crystals, and 3.64 for the prismatic crystals. E. Birk and W. Biltz gave 3.791 at  $15^\circ/4^\circ$  for crystals dehydrated at a dull red-heat; G. L. Clark and co-workers, 3.710 at  $25^\circ/4^\circ$  for crystals dehydrated at  $280^\circ$ ; and E. Moles and M. Crespi, 3.666 at  $25^\circ/4^\circ$  for crystals dehydrated at  $350^\circ$ . H. Schiff gave 1.924 for the sp. gr. of crystals of the heptahydrate; O. Pettersson, 1.958 and 1.964 for crystals at  $15.5^\circ$  to  $15.6^\circ$ ; H. Schröder, 1.958; E. Gunther, 1.938; B. Gossner, 1.948; G. L. Clark and co-workers, 1.948 at  $24^\circ/5^\circ$ ; M. H. Belz, 1.950; E. Widmer, 1.96 at  $18^\circ$  to  $21^\circ$ ; and E. Moles and M. Crespi, 1.930 at  $25^\circ/4^\circ$ . H. G. K. Westenbrink calculated the sp. gr. to be 1.889 from the lattice constants. For the hexahydrate, T. E. Thorpe and J. I. Watts gave 2.019 at  $15^\circ/15^\circ$ ; B. Gossner, 2.000; and G. L. Clark and co-workers, 2.029 at  $25^\circ/34^\circ$ . For the pentahydrate, T. E. Thorpe and J. I. Watts, and L. Playfair gave 2.134; and E. Widmer, 2.2 at  $18^\circ$  to  $21^\circ$ . For the tetrahydrate, T. E. Thorpe and J. I. Watts gave 2.327 at  $15^\circ/15^\circ$ . For the dihydrate, T. E. Thorpe and J. I. Watts, and L. Playfair gave 2.712. For the monohydrate, T. E. Thorpe and J. I. Watts gave 3.125 at  $15^\circ/15^\circ$ ; and E. Moles and M. Crespi, 3.076 at  $25^\circ/4^\circ$ . Determinations of the sp. gr. of aq. soln. were made by G. Charpy, F. Dreyer, A. M. Morrison, J. Wagner, W. W. J. Nicol, G. Quincke, R. W. Roberts, R. C. Cantelo and A. J. Berger, G. Jäger and H. Decker, W. Manchot and co-workers, and J. N. Rakshit. The *International Critical Tables* gave for soln. with C per cent. of  $\text{CoSO}_4$ :

C.	.	.	.	1	2	4	6	8 per cent.
Sp. gr.	{	$0^\circ$	:	1.0107	1.0215	1.0436	1.0662	1.0890
		$25^\circ$	:	1.0072	1.0174	1.0380	1.0588	1.0800

B. Cabrera and co-workers gave for 0.2212 per cent. soln.,  $1.2638\{1-0.0327(\theta-20)\}$ , and for 0.1478 per cent. soln.,  $1.1649\{1-0.0326(\theta-20)\}$ . The **molecular volume**

of the salt was discussed by E. N. Gapon, R. C. Cantelo and H. E. Phifer, and J. A. Groshans. T. E. Thorpe and J. I. Watts studied the sp. vol. of cobalt sulphate and of its hydrates; E. Moles and M. Crespi, the mol. vol. of the water of hydration; and E. N. Gapon, the relation between the sp. gr., the m.p., and the ionization of salts. A. Baladin, and H. H. Stephenson studied the contraction which occurs in the formation of the anhydrous salt from its elements; A. Baladin, H. H. Stephenson, J. N. Rakshit, and G. L. Clark and co-workers, the contraction during the formation of the heptahydrate from the anhydrous salt and water; G. L. Clark and co-workers, and J. N. Rakshit, the contraction which occurs during the formation of the hexahydrate; J. N. Rakshit, the pentahydrate; G. L. Clark and co-workers, and J. N. Rakshit, the tetrahydrate; and J. N. Rakshit, the monohydrate. C. Charpy, and J. N. Rakshit studied the vol. contraction of the anhydrous salt when it is dissolved in water. F. Dreyer gave for the temp. of maximum density of aq. soln. with  $C$  per cent. of cobalt sulphate:

$C$	0	0.181	0.366	0.735	1.536	1.823 per cent.
Temp.	3.96°	3.70°	3.44°	2.92°	1.78°	1.43°

M. Torre measured the rate of **diffusion** of cobalt sulphate in water and found for the change in concentration, in grams of  $\text{CoSO}_4$  per 100 c.c., after 24 hrs., with an initial conc. of:

Rate of diffusion	0.775 grm. per 100 c.c.			0.155 grm. per 100 c.c.		
	30°	40°	50°	30°	40°	50°
	0.194	0.322	0.450	0.041	0.065	0.087

E. Dittler discussed the diffusion of the salt in the crystalline form; and J. J. Coleman, aq. soln. G. Tammann discussed the relation of the mol. attraction to the **internal pressure**; S. Oka, the **surface tension** of the soln.; and Z. H. Skraup and co-workers, the capillary rise of the soln. in paper. R. C. Cantelo and A. J. Berger, and O. Pulvermacher made observations on the **viscosity**, and J. Wagner found for the relative values of the viscosity, water unity, at 25°:

$\text{CoSO}_4$	$N$	0.5 $N$	0.25 $N$	0.125 $N$
$\eta$	1.3543	1.1590	1.0766	1.0402

and for soln. containing:

$\eta$	21.167 per cent. $\text{CoSO}_4$				7.239 per cent. $\text{CoSO}_4$			
	15°	25°	35°	45°	15°	25°	35°	45°
	1.9360	1.4620	1.1300	0.8995	0.8672	0.6872	0.5496	0.4508

H. Kopp found the **specific heat** of the heptahydrate between 15° and 80° to be 0.343. K. Jauch, and N. de Kolossowsky studied the subject. W. A. Tilden gave 96° to 98° for the **melting-point** of the heptahydrate; and E. N. Gapon studied the relation between the sp. gr., the m.p., and the ionization. L. Kahlenberg found the **lowering of the freezing-point** of aq. soln. containing 1.457 and 14.143 grms. of  $\text{CoSO}_4$  per 100 grms. of water to be, respectively, 0.209° and 1.587°; and for soln. with 0.879, 10.54, and 17.58 grms., H. C. Jones and F. H. Getman gave, respectively, 0.143°, 1.187°, and 2.073°. Observations were made by F. Dreyer, and N. Tarugi and G. Bombardini. L. Kahlenberg measured the **raising of the boiling-point** of aq. soln. with 4.446, 9.596, 20.60, and 32.84 grms. of  $\text{CoSO}_4$  per 100 grms. of water, and found, respectively, 0.110°, 0.262°, 0.568°, and 1.055°.

G. Wiedemann, W. Müller-Erzbach, and H. Lescœur measured the **vapour pressure** of the heptahydrate,  $p$  mm., and C. D. Carpenter and E. R. Jette observed:

$p$	25.00°	40.18°	45.07°	45.17°	50.16°	55.29°	60.22°	65.16°	70.16°
	17.0	48.1	66.0	66.5	84.9	107.7	134.9	167.3	204.3

there is a transition point at 45.1°, where the vap. press. of the hepta- and the hexahydrates and of a sat. soln. are the same. Observations were made by W. C. Schumb. A. P. Rostkowsky gave for the heptahydrate, and the hexahydrate,

18 mm. at 25°. He observed evidence of the existence of only the hepta-, hexa-, and monohydrates. G. Tammann found the lowering of the vap. press. of aq. soln. with 10.55, 28.89, and 52.16 grms.  $\text{CoSO}_4$  per 100 grms. of water to be, respectively, 7.5, 20.4, and 54.2 mm. Observations were also made by H. Lescœur, and I. Bencowitz and H. T. Hotchkiss. C. C. Tanner studied Sorét's effect.

H. Baubigny and E. Péchard, and M. A. Rakuzin and D. A. Brodsky found that the **dehydration** of the heptahydrate readily occurs, with the loss of a mol. of water, to form the hexahydrate, by exposure to dry air; and L. de Boisbaudron noted that gentle warming of the heptahydrate has a similar result. M. A. Rakuzin and D. A. Brodsky observed that the dihydrate is formed over sulphuric acid. L. Hackspill and A. P. Kieffer, F. Krafft, and A. Adolphs found that the monohydrate is formed in vacuo over phosphorus pentoxide. T. E. Thorpe and J. I. Watts found that the heptahydrate is completely dehydrated at 250°, and that at 100°, the heptahydrate passes into the monohydrate. Observations were made by A. Étard, G. Vortmann, C. Gaudefroy, and M. Copisarow. F. Krafft said that the seventh mol. of water is retained by exposing the salt in the vacuum required for producing the cathode light. When gently heated in a current of dry air, the hydrated sulphate was found by H. O. Hofman and W. Wanjukoff to become anhydrous at 276°; E. Moles and M. Crespi said 220° to 260°; and for complete dehydration, A. Adolphs, K. Friedrich and co-workers, and L. Hackspill and A. P. Kieffer recommended 300° to 420° for complete dehydration—*vide supra*. P. Théodoridès gave 275° for the transition temp. of the monohydrate to the anhydrous sulphate.

P. Klobb observed no change in the anhydrous sulphate at ordinary temp., but at high temp., F. A. C. Gren, and J. C. G. de Marignac noted that the salt is decomposed into cobalt oxide, sulphur dioxide, and oxygen. According to J. L. Proust, the crystals of the heptahydrate give off water when heated, and become rose-coloured, but they do not lose sulphur trioxide at a red-heat. A. Ditte said that the **thermal decomposition** of the sulphate begins at 440°; G. Marchal, 690°; J. A. Hedvall and J. Heuberger, 940°; and K. Friedrich and A. Blickle gave 880° for the temp. of decomposition; and K. Flick, 905°, and 760 mm. press. W. N. Hartley observed that there is no evidence of decomposition at 300°, and that salt becomes lilac-coloured between 500° and a red-heat, but, on cooling, the original red colour of the salt is restored. O. Barth found the anhydrous sulphate to be stable at 600°; 3.4 per cent. decomposition can be detected after heating 3 hrs. at 615°; and complete decomposition occurred after heating 2 hrs. at 735°. H. O. Hofman and W. Wanjukoff gave 692° for the beginning of dissociation, and 720° to 770° for the temp. of complete dissociation. R. Schenck and E. Raub observed that the dissociation press. for  $2\text{CoSO}_4 = 2\text{CoO} + 2\text{SO}_2 + \text{O}_2$ , rises very rapidly in the vicinity of 900°. The temp. of decomposition is lowered appreciably in the presence of porcelain sherds. G. Marchal observed that the decomposition of the sulphate begins at about 690°, and that the partial press. of the gaseous constituents,  $p$  mm., and the total press.,  $P$  mm., are:

	720°	800°	845°	900°	950°	1000°	1030°
$P$	1.15	3.8	9.18	29.1	67.4	144	217.7
$p_{\text{SO}_3}$	0.1	0.25	0.69	2.18	8.17	11.25	17.08
$p_{\text{SO}_2}$	0.7	2.36	6.07	17.95	41.49	88.50	133.74
$p_{\text{O}_2}$	0.35	1.18	3.03	8.97	20.74	44.25	66.87

H. H. Willard and R. D. Fowler based a method of separating the metals on the differences in the rates of thermal decomposition.

J. Thomsen gave for the **heat of formation**  $(\text{Co}, \text{H}_2\text{SO}_4\text{Aq.}) = 19.71$  Cals.;  $(\text{Co}, \frac{1}{2}\text{O}_2, \text{H}_2\text{SO}_4\text{Aq.}) = 88.07$  Cals.;  $(\text{Co}, \text{O}_2, \text{SO}_2, 7\text{H}_2\text{O}) = 162.97$  Cals.; and M. Berthelot gave  $(\text{Co}, \text{S}, 2\text{O}_2, 7\text{H}_2\text{O}) = 234.05$  Cals. R. Schenck and E. Raub gave 228.8 Cals. for the heat of formation of  $\text{CoSO}_4$ . J. Thomsen gave for the **heat of neutralization**  $(\frac{1}{2}\text{Co}(\text{OH})_2, \frac{1}{2}\text{H}_2\text{SO}_4) = 12.336$  Cals. G. Marchal gave 50.6 Cals. for the **heat of dissociation** of the anhydrous sulphate between 820° and 950°. J. Thomsen



gave for the **heat of solution** of a mol of the heptahydrate in 800 mols of water,  $-3.57$  Cals.; and P. A. Favre and C. A. Valson gave  $-1.68$  Cals. for the heat of soln. of the heptahydrate. T. E. Thorpe and J. I. Watts studied the relation between the sp. vol. of the various hydrates and the heat of soln.

The **index of refraction** of the heptahydrate was found by E. Widmer for Na-light to be  $1.483$ , and the molecular refraction  $55.68$ . According to E. S. Larsen and M. L. Glenn, the indices of refraction of the monoclinic heptahydrate are  $\alpha=1.477$ ,  $\beta=1.483$ , and  $\gamma=1.489$ , the dispersion is feeble, and the optical character is negative. M. W. Porter gave  $\alpha=1.4748$ ,  $\beta=1.4820$ , and  $\gamma=1.4885$ . E. S. Larsen and M. L. Glenn gave for the uniaxial hexahydrate,  $\alpha=1.531$ ,  $\beta=1.549$ , and  $\gamma=1.552$ , and the optical character is negative. They gave for the triclinic pentahydrate,  $\alpha=1.529$ ,  $\beta=1.546$ , and  $\gamma=1.548$ , and the optical character is negative. E. Widmer gave for the mean value in Na-light,  $1.545$ , and for the mol. refraction,  $35.17$ . The fibrous monohydrate has  $\alpha=1.600$ , and  $\gamma=1.645$ , and the crystals  $\alpha=1.603$ ,  $\beta=1.639$ , and  $\gamma=1.683$ , and the optical character is positive. H. C. Jones and F. H. Getman measured the index of refraction of aq. soln. with  $C$  mols of  $\text{CoSO}_4$  per litre, and found :

$C$ . . .	0.0567	0.2267	0.6799	0.9066	1.1199	1.1333
$\mu$ . . .	1.32751	1.33248	1.34423	1.34974	1.35240	1.35588

Measurements were also made by L. R. Ingersoll, and R. W. Roberts. Observations on the **magnetic rotation** of the plane of polarization of aq. soln. were made by R. Wacksmuth, L. R. Ingersoll, M. Schérer and R. Cordonnier, F. Allison and E. J. Murphy, R. W. Roberts, and E. Miescher. W. Ackroyd and H. B. Knowles said that the heptahydrate is almost opaque to the **X-rays**. R. Robl observed no luminescence in **ultra-violet light**; and M. Trautz, no **triboluminescence**. T. Svensson studied the **photoelectric effect** with soln. of the sulphate; and P. Niggli, the reflexion maxima.

According to W. N. Hartley, the **colour** of the anhydrous sulphate is rose-red, or, according to G. L. Clark and co-workers, lavender-red. W. N. Hartley observed that the rose-red colour persists at  $300^\circ$ , but at  $500^\circ$  to a red-heat, it becomes lilac, and decomposition then begins. The original colours of the sulphate return on cooling. The presence of traces of nitrate, chloride, or ammonium salts make the salt red. Hot, conc. sulphuric acid does not change the colour of the salt, although F. G. Donnan and H. Bassett said that the boiling acid imparts a bluish tinge. M. Bamberger and R. Grengg observed that the colour of the heptahydrate at ordinary temp., is dark red; but at  $-190^\circ$ , the colour is pale yellowish-red. A. H. Pfund added that there is a maximum reflection in the ultra-red at  $9.05\mu$ . The colour of dil. aq. soln. is rose-red, and that of conc. soln. is a deep red. H. M. Vernon, and M. Kahanowicz and P. Orecchioni studied the changes in colour which occur on dilution, and on raising the temp., when the colour becomes blue—*vide supra*, the colour of cobaltous chloride. The colour, and **absorption spectra** of soln. of cobalt sulphate were examined by P. Bovis, F. L. Cooper, A. Étard, A. Hantzsch, J. Hildebrand, R. Hill and O. R. Howell, R. A. Houstoun and co-workers, H. C. Jones and co-workers, J. Lifschitz and E. Rosenbohm, B. E. Moore, R. W. Roberts and co-workers, W. J. Russell, and P. Vaillant. A. Müller discussed the colour of a mixed soln. of cobalt and nickel sulphates.

E. Franke found the eq. **electrical conductivity**,  $\lambda$ , of soln. with a gram equivalent of the salt in  $v$  litres, at  $25^\circ$ , to be :

$v$ . . .	32	62	128	256	512	1064
$\lambda$ . . .	62.35	72.45	81.88	91.68	100.6	108.0

Observations were made by P. D. Chroustschoff, N. Tarugi and G. Bombardini, G. Vicentini, and R. C. Cantelo and A. J. Berger. H. H. Hosford and H. C. Jones, and H. C. Jones and co-workers gave for the mol. conductivity,  $\mu$ , of soln. with a mol of the salt in  $v$  litres, when the temp. coeff. is  $a$ , and the degree of ionization,  $\alpha$  :

$v$	2	16	32	128	512	1024	2048
$\mu \left\{ \begin{array}{l} 0^\circ \\ 25^\circ \end{array} \right.$	29.47 55.10	49.26 91.97	56.26 105.4	75.89 143.4	94.88 180.2	101.9 196.9	110.9 214.1
$\alpha \left\{ \begin{array}{l} 0^\circ-10^\circ \\ 10^\circ-25^\circ \end{array} \right.$	0.97 1.06	1.63 1.76	1.88 2.02	2.56 2.79	3.21 3.55	3.57 3.95	3.75 4.38
$\alpha \left\{ \begin{array}{l} 25^\circ-35^\circ \\ 0^\circ \end{array} \right.$	1.04 26.6	1.74 44.4	2.04 50.7	2.87 68.4	3.79 85.6	4.23 91.9	4.51 100.0
$\alpha \left\{ \begin{array}{l} 25^\circ \end{array} \right.$	25.7	43.0	49.2	67.0	84.2	92.0	100.0

R. C. Cantelo and E. C. Payne found that the **transport numbers**,  $n$ , of cobalt  $\text{Co}^{++}$ , in soln. of cobalt sulphate, are :

$N\text{-CoSO}_4$	0.233	0.753	1.444	1.860	2.833	3.994
$n$	0.396	0.373	0.316	0.286	0.260	0.149

It is assumed that complex ions are formed, and that the decreasing value of the transport numbers corresponds with an increase in the amounts of cobalt carried to the anode as complex ions. The subject was studied by R. W. Money and C. W. Davies, and H. C. Jones and co-workers. P. Vaillant calculated the **degree of ionization**,  $\alpha$  per cent., from the conductivity data—*vide supra*. According to H. G. Denham, the degrees of **hydrolysis** and the  **$\text{H}^+$ -ion concentration** of aq. soln. with a mol of the salt in  $v$  litres, at  $25^\circ$ , are :

$v$	2	4	8	16	32
$[\text{H}^+] \times 10^4$	0.313	0.210	0.163	0.107	0.093
Hydrolysis	0.0031	0.0042	0.0065	0.0085	0.0149

The hydrolysis with nickel sulphate is greater than with cobalt sulphate. M. le Blanc, P. Baumann, S. Labendzinsky; A. Coehn and M. Gläser, and H. W. Toepffer studied the **decomposition potential** of soln. of cobalt sulphate, and noted the anodic oxide formation at 1.248 volts with  $N\text{-CoSO}_4$ , and the evolution of oxygen at 1.448 volts. A. Coehn and M. Gläser found that in slightly alkaline soln., cobalt sulphate furnishes oxide at 1.21 volts; and in slightly acidic soln., cobalt oxide is deposited on the anode at 1.52 volts; and in more strongly acidic soln., no oxide is deposited. The deposited oxide has the composition  $\text{Co}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ —with thin deposits,  $n=2$ , and with thick deposits,  $n=3$ . H. T. Kalmus and co-workers gave 2.16 volts for the decomposition potential of  $N\text{-CoSO}_4$  with platinum electrodes; K. F. Ochs studied the **electromotive force** of the cells  $\text{Pt}_{\text{platinized}} | \text{CoSO}_4, \text{H}_2\text{SO}_3 | \text{KI}, \text{I} | \text{Pt}$ , and  $\text{Pt}_{\text{platinized}} | \text{CoSO}_4, \text{H}_2\text{O}_2, \text{H}_2\text{SO}_4 | \text{KI}, \text{I} | \text{Pt}$ ; and H. G. Denham, the cell  $\text{H}_2 | \text{CoSO}_4\text{aq.} | \text{NH}_4\text{NO}_3\text{aq.} | \text{Hg}_2\text{Cl}_2 | \text{Hg}$ . H. Fresenius and F. Bergmann, and A. Gaiffe studied the **electrolysis** of soln. of cobalt sulphate with platinum electrodes—*vide supra*—and E. S. Hedges noted periodic fluctuations of the potential. J. Lifschitz observed the **Becquerel effect**. R. Saxon made some observations on the electrolysis of these soln.; and A. N. Schtschukareff studied the magnetic effect which occurs in the electrolysis of soln. of the sulphate.

The **magnetic properties** of the anhydrous sulphate were studied by G. Wiedemann, P. Plessner, P. Weiss and G. Foëx, E. Feytis, G. Jäger and H. Decker, M. H. Belz, A. Chatillon, R. Hocart and A. Serres, P. Krishnamurti, P. Hausknecht, T. Ishiwara, and K. Honda and T. Ishiwara. P. Théodoridès gave for the **magnetic susceptibility** of the anhydrous sulphate,  $\chi = 62.25 \times 10^{-6}$  mass unit; A. Serres gave :

$\chi \times 10^6$	280.5° 66.91	364.5° 53.31	476.6° 42.10	594.6° 34.29	695.4° 29.75	728.5° 28.46
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and L. C. Jackson :

$\chi \times 10^6$	16.5° 62.21	-103.35° 96.96	-195.73° 169.7	-252.55° 378.8	-255.56° 420.7	-258.23° 461.8
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According to P. Théodoridès, A. Chatillon, and A. Serres, the Curie point is near  $0^\circ$ ; P. Théodoridès observed an irregularity in the curve at  $275^\circ$  corresponding with the transformation of the monohydrate into the anhydrous salt. Observations

were made by T. Ishiwara, P. C. Ray and H. Bhar, N. S. Krishnan and co-workers, P. Weiss, B. Cabrera and co-workers, and L. C. Jackson and H. K. Onnes. G. Meslin gave  $73.6 \times 10^{-6}$  vol. unit for the magnetic susceptibility of the heptahydrate; and W. Finke gave  $70.9 \times 10^{-6}$  vol. unit in the direction of the  $a$ -axis,  $64.0 \times 10^{-6}$  vol. unit in the direction of the  $b$ -axis, and  $68.5 \times 10^{-6}$  vol. unit in the direction of the  $c$ -axis. P. Weiss and G. Foëx gave for the sp. susceptibility,  $\chi = 31.9 \times 10^{-6}$  mass unit at  $20^\circ$ ; M. H. Belz,  $33.85 \times 10^{-6}$  mass unit at  $16^\circ$ . E. Feytis, L. C. Jackson and H. K. Onnes, A. A. Lutheroth, P. Weiss and E. D. Bruins, P. Weiss and G. Foëx, and B. Cabrera made observations on the subject; and L. C. Jackson gave:

	$19^\circ$	$-103.5^\circ$	$-195.7^\circ$	$-209.2^\circ$	$-252.6^\circ$	$-258.24^\circ$
$\chi \times 10^6$	37.0	61.6	126.9	144.6	403.0	535.9

L. C. Jackson's results for the reciprocal mol. susceptibility of the heptahydrate and the anhydrous salt are summarized in Fig. 120.

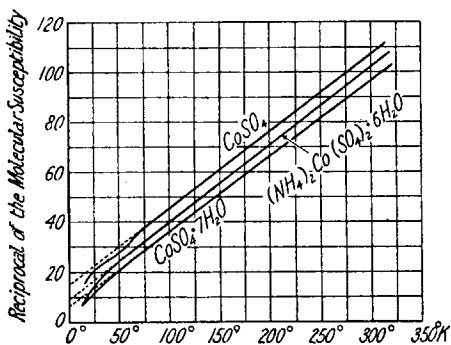


FIG. 120.—The Effect of Temperature on the Reciprocal Molecular Magnetic Susceptibility.

effect of the concentration of the soln. on the magnetic properties; and G. Jäger and H. Decker gave for soln. with  $C$  per cent. of  $\text{CoSO}_4$ , at  $20^\circ$ :

$C$	1.172	0.938	0.703	0.293	0.117	0.023 per cent.
$\chi \times 10^{-6}$	-0.0032	-0.1419	-0.2805	-0.5340	-0.6456	-0.7148

The magneton numbers of the anhydrous salt were discussed by B. Cabrera, A. Chatillon, G. Foëx, L. C. Jackson, A. Serres, P. Théodoridès, and P. Weiss and G. Foëx; those of the heptahydrate, by B. Cabrera, and L. C. Jackson and co-workers; and those of the aq. soln., by A. Chatillon, A. Quartaroli, R. H. Weber, and P. Weiss and G. Foëx. The magnetic moment of the anhydrous salt was discussed by K. Honda and T. Ishiwara. W. Sucksmith studied the gyromagnetic effect. H. E. Armstrong and E. H. Rodd, and G. Roasio observed the orientation of the crystals of the heptahydrate grown in a magnetic field; and W. König, the effect of the deformation of gelatin cylinders containing the salt.

G. P. Schweder found that when the sulphate is heated in hydrogen, it is reduced to sulphide, provided the temp. is not too high; J. H. Weibel studied the reaction; and S. Miyamoto observed the reduction with hydrogen and the silent discharge. According to J. L. Proust, the crystals of the heptahydrate have a faintly astringent, slightly bitter, metallic taste; and G. Vortmann noted that the anhydrous salt in air is very hygroscopic. The heptahydrate effloresces in dry air, as previously indicated. E. S. Larsen and M. L. Glenn, H. Baubigny and E. Péchard, and A. P. Rostkowsky also noted the efflorescence of the hexahydrate in dry air. G. Vortmann noted that the monohydrate is rather less hygroscopic than the anhydrous salt. P. Klobb noted that the sulphate is not chemically changed by exposure to air at ordinary temp. A. Mailfert observed that with ozone, sulphuric

acid and a peroxide are formed. E. Brunner studied the oxidation of aq. soln. by ozone.

F. A. C. Gren, P. Klobb, and C. Lepierre and M. Lachaud noted that the anhydrous sulphate dissolves slowly in boiling water; and G. Vortmann added that the monohydrate dissolves more slowly than the anhydrous salt. G. J. Mulder, C. von Hauer, E. Tobler, C. L. Wagner, R. M. Caven and W. Johnston, C. Montemartini and L. Losana, A. and H. Benrath, and I. Koppel and H. Wetzel measured the solubility of cobalt sulphate,  $S$  grms. of  $\text{CoSO}_4$  in 100 grms. of soln., and their results correspond with:

	0°	10°	20°	30°	40°	50°	60°	70°	80°	100°
$S$ .	20.35	23.40	26.58	29.70	32.81	35.56	37.65	39.66	41.18	45.35

I. Koppel and H. Wetzel, in agreement with J. C. G. de Marignac, said that the heptahydrate is the solid phase up to  $40.7^\circ$ , when it passes into the hexahydrate. C. D. Carpenter and E. R. Jette gave  $45.1$  for this transition point; and A. P. Rostkowsky observed only the three hydrates—hepta-, hexa-, and monohydrates. P. Théodorides gave  $215^\circ$  for the transition temp.,  $\text{CoSO}_4 \cdot \text{H}_2\text{O} \rightleftharpoons \text{CoSO}_4 + \text{H}_2\text{O}$ , based on magnetic observations; I. Koppel and H. Wetzel gave  $-3.0^\circ$  for the eutectic temp. of the heptahydrate. A. Étard observed a decreasing solubility with a rise of temp. above  $100$ , and a soln. sat. at  $15^\circ$  begins to deposit a solid at about  $145^\circ$ , so that at  $220^\circ$  the soln. contains only 1 per cent. of salt, and at  $250^\circ$  the amount of salt in soln. approaches zero. According to K. Jableczynsky and co-workers, the rate of dissolution of the hydrate in water and non-aqueous solvents follows the rule characteristic of that for the less soluble solids. D. N. Bhattacharyya and N. R. Dhar, and N. R. Dhar noted the tendency of the salt to form supersaturated soln.

As indicated above, the salt is slightly hydrolyzed in aq. soln. A number of basic salts have been reported, although there is little to show which are chemical individuals, and which are mixtures. According to H. Fuchs, when cobaltous hydroxide is shaken with soln. of cobalt sulphate, until equilibrium is attained, the conc. of the soln. attains 25 grms. in 100 grms. of water, the solid phase assumes a constant composition for concentrations up to 30 grms. of cobalt sulphate per 100 grms. of water, and approximates **cobalt tetroxysulphate**,  $\text{CoSO}_4 \cdot 4\text{CoO} \cdot 14\text{H}_2\text{O}$ , or  $[(\text{H}_2\text{O} \cdot \text{H}_2\text{O})_2 \cdot \text{Co} \cdot (\text{OCo} \cdot \text{H}_2\text{O} \cdot \text{H}_2\text{O})_4] \text{SO}_4 (\text{H}_2\text{O})_2$ , in accord with the observations on the vap. press. of the *tetradecahydrate* that 4 mols. of water are lost over conc. sulphuric acid, to furnish the *decahydrate*,  $[(\text{H}_2\text{O} \cdot \text{H}_2\text{O})_2 \cdot \text{Co} \cdot (\text{OCo} \cdot \text{H}_2\text{O})_4] \text{SO}_4 (\text{H}_2\text{O})_2$ . At  $100^\circ$ , 4 mols. of water were lost in 7 hrs., and  $[(\text{H}_2\text{O})_4 \cdot \text{Co} \cdot (\text{OCo} \cdot \text{H}_2\text{O})_2] \text{SO}_4 (\text{H}_2\text{O})_2$  was formed. S. U. Pickering reported **cobalt trioxysulphate**,  $4\text{CoO} \cdot \text{SO}_3$ , to be formed by adding alkali-lye to soln. of cobalt sulphate. J. Habermann reported cobalt tetroxysulphate,  $\text{CoSO}_4 \cdot 4\text{CoO} \cdot 4\text{H}_2\text{O}$ , to be formed by adding aq. ammonia gradually to a boiling, neutral soln. of cobalt sulphate. The blue, flocculent precipitate is stable at ordinary temp. It loses some water at  $150^\circ$ , and all is lost at  $288^\circ$  to  $292^\circ$ , to furnish  $5\text{CoO} \cdot \text{SO}_3$ . W. Feitknecht found that the lattice of the salt of the type  $\text{CoSO}_4 \cdot 3\text{Co}(\text{OH})_2$ , consists of alternate layers of the normal salt and hydroxide. D. Strömholm reported **cobalt pentoxysulphate**,  $6\text{CoO} \cdot \text{SO}_3 \cdot n\text{H}_2\text{O}$ , to be formed by adding sodium hydroxide, carbonate, or hydrocarbonate to a soln. of cobalt sulphate; and N. Athanasesco, the decahydrate,  $6\text{CoO} \cdot \text{SO}_3 \cdot 10\text{H}_2\text{O}$ , as a bluish-green, crystalline powder, by boiling an aq. soln. of 5 grms. of cobalt sulphate with 1 or 2 grms. of calcium or barium carbonate, for 6 to 8 hrs., evaporating the liquid down to 40 c.c., and then heating the product in a sealed tube at  $200^\circ$ . A. Bernardi found that cobaltous sulphate behaves like the chloride (*q.v.*) towards sodium hydroxide, producing a green precipitate. R. Kuhn and A. Wassermann studied the action of the sulphate on **hydrogen dioxide**.

H. Wolfmann found that the salt in soln. in dil. sulphuric acid is oxidized by **fluorine** to cobaltic sulphate. F. Ephraim, and C. Hensigen observed that **hydrogen**

**chloride** does not attack anhydrous cobalt sulphate at ordinary temp. S. E. Moody found that the salt in boiling, aq. soln. is hydrolyzed by a mixture of **potassium iodide and iodate**:  $3\text{CoSO}_4 + 5\text{KI} + \text{KIO}_3 + 3\text{H}_2\text{O} = 3\text{Co(OH)}_2 + 3\text{K}_2\text{SO}_4 + 3\text{I}_2$ . S. S. Bhatnagar and co-workers said that the reaction is not influenced by a magnetic field. Unlike ferrous hydroxide similarly formed, the precipitated cobaltous hydroxide is not oxidized. The action of **hydrogen sulphide** on a soln. of the salt was studied by G. Bruni and M. Padoa, and H. Baubigny and E. Péchard—*vide supra*. C. Montemartini and L. Losana studied the system with **sulphuric acid** and cobalt sulphate. H. Brintzinger and H. Osswald studied the complex sulphates,  $[\text{Co}_2(\text{SO}_3)_4]^{4-}$ . J. T. Norton found that when the sulphate is heated with **sodium thiosulphate** in a sealed tube, at  $140^\circ$  to  $200^\circ$ , cobalt sulphide and sulphur are formed. C. Dufraisse and D. Nakae studied the catalytic oxidation of soln. of **sodium sulphite** in the presence of cobalt sulphate. C. Montemartini and L. Losana studied the solubility of the salt in **sulphuric acid**, and in soln. of potassium sulphate; and A. B. Prescott, the decomposition of the sulphate by hydrochloric acid. C. Montemartini and L. Losana observed the formation of **cobalt hydrosulphate**,  $\text{CoSO}_4\cdot\text{H}_2\text{SO}_4$ , or  $\text{Co}(\text{HSO}_4)_2$ .

G. Gore, and E. C. Franklin and C. A. Kraus noted that anhydrous cobalt sulphate is insoluble in liquid **ammonia**. W. R. Hodgkinson and C. C. Trench studied the reduction of the sulphate heated in ammonia gas. H. Rose observed that the sulphate vigorously absorbs ammonia, to form **cobaltous hexamminosulphate**,  $\text{CoSO}_4\cdot 6\text{NH}_3$ . The reaction is accompanied by the evolution of heat, to form a pale red, voluminous powder. The compound was also prepared by M. A. Rakuzin and D. A. Brodsky, G. L. Clark and co-workers, and E. Birk and W. Biltz. F. Ephraim said that the reaction is favoured by the condensation of the ammonia. E. Frémy obtained it by the action of ammonia on a conc., aq. soln. of cobalt sulphate while air is excluded, and then precipitating the salt with alcohol. E. Birk and W. Biltz found the sp. gr. to be 1.6545 at  $25^\circ/4^\circ$ , and the mol. vol. 155.5. F. Ephraim discussed the mol. vol. of the contained ammonia; and the dissociation press. of the ammonia,  $p$  mm., was found to be:

	$66^\circ$	$80.5^\circ$	$90^\circ$	$98.5^\circ$	$102.5^\circ$	$106^\circ$	$109.5^\circ$
$p$	87	174	292	414	484	538	596

so that the dissociation temp. at 760 mm. works out to be  $389.5^\circ$ ; the calculated heat of formation is 73.9 Cals. per mol. of  $\text{NH}_3$ . The powder is electrified when shaken. According to H. Rose, the salt is readily soluble in aq. ammonia; but it is hydrolyzed by water. When heated to redness, the salt melts, turns blue, evolves much ammonia, and gives a small sublimate of ammonium sulphite. D. M. Bose studied the magnetic properties; and G. Wiedemann found that the magnetic susceptibility is similar to that of ammonium cobaltous sulphate.

According to F. Ephraim, there is evidence of the formation of a higher ammine, probably the **decammine**, at very low temp. The **pentammine**, described by G. L. Clark and co-workers, could not be prepared by F. Ephraim. At temp. between  $106^\circ$  and  $116^\circ$ , the hexammine passes into violet-rose **cobaltous tetramminosulphate**,  $\text{CoSO}_4\cdot 4\text{NH}_3$ . The dissociation press. of the tetrammine at  $113.5^\circ$ ,  $124^\circ$ , and  $135^\circ$  are, respectively, 210, 404, and 656 mm., so that the dissociation temp. at 760 mm. is  $409.5^\circ$ . The heat of formation is 14.78 Cals. per mol. of ammonia. G. L. Clark and co-workers reported **cobaltous diaquotetramminosulphate**,  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{SO}_4$ , to be formed by passing ammonia into a hot, conc. soln. of cobaltous sulphate, and subsequently cooling the liquid; or by heating a mixture of 20 grms. of hydrated cobaltous sulphate, 40 c.c. of conc., aq. ammonia, and 10 c.c. of alcohol in a press. flask heated on a water-bath. The red crystals have a sp. gr. 1.804; and mol. vol. 143.67; and they are stable in dry air, but oxidize in moist air. F. Ephraim observed the formation of what is possibly **cobaltous triamminosulphate**,  $\text{CoSO}_4\cdot 3\text{NH}_3$ , by heating a higher ammine between  $132^\circ$  and  $135^\circ$ , and **cobaltous diamminosulphate**,  $\text{CoSO}_4\cdot 2\text{NH}_3$ , by heating a

higher ammine at 254°. The dissociation press. of the violet powder at 147° is 40 mm. If a higher ammine be heated between 254° and 257°, **cobaltous hemiamminosulphate**,  $\text{CoSO}_4 \cdot \frac{1}{2}\text{NH}_3$ , is formed. Its dissociation temp. exceeds 320°. G. Poma added a soln. of cobalt sulphate to a soln. of potassium iodide saturated with ammonia, and obtained rose-red **potassium cobaltous hexamminodiiodosulphate**,  $2\text{KI} \cdot \text{CoSO}_4 \cdot 6\text{NH}_3$ , which is easily oxidized in air; he also obtained the analogous **potassium cobaltous hexamminodibromosulphate**,  $2\text{KBr} \cdot \text{CoSO}_4 \cdot 6\text{NH}_3$ . O. R. Foz and L. de Boucher studied the amminosulphates.

T. Curtius and F. Schrader observed that a flesh-coloured precipitate is formed when **hydrazine hydrate** is added to a soln. of cobalt sulphate; and H. Franzen and O. von Mayer prepared **cobaltous trihydrazinesulphate**,  $\text{CoSO}_4 \cdot 3\text{N}_2\text{H}_4$ , in a similar manner. The buff, crystalline powder is insoluble in water; it is decomposed by boiling water; and is readily soluble in dil. acids and in aq. ammonia. P. C. Ray and H. Bhar found the magnetic susceptibility at 26° to be  $35.9 \times 10^{-6}$  mass unit. W. Feldt observed that when a soln. of **hydroxylamine sulphate** and cobaltous sulphate, in an atm. of hydrogen, is treated with an alcoholic soln. of hydroxylamine, rose-red, acicular crystals of **cobaltous diaquohydroxylamine-sulphate**,  $\text{CoSO}_4 \cdot \text{NH}_2\text{OH} \cdot 2\text{H}_2\text{O}$ , are formed. The salt is insoluble in cold water, but soluble in hot water. The hot, aq. soln. is quickly oxidized. W. Manchot and co-workers found that soln. with 12.217 and 24.433 grms. of  $\text{CoSO}_4$  per 100 c.c. dissolve, respectively, 27.8 and 17.5 c.c. of **nitrous oxide**. F. L. Usher, and G. Hüfner studied the absorption of **nitric oxide** by soln. of cobalt sulphate. P. C. and N. Ray obtained a complex **cobaltous ethylphosphonium sulphate**,  $\text{CoSO}_4 \cdot \{(\text{C}_2\text{H}_5)_4\text{P}\}_2\text{SO}_4 \cdot 8\text{H}_2\text{O}$ . A. V. Pavlinova studied the oxidation of ammoniacal solutions of **arsenites** in presence of cobaltous sulphate as catalyst.

W. Manchot and co-workers found that soln. with 12.356 and 24.712 grms. of  $\text{CoSO}_4$  per 100 c.c. dissolve, respectively, 0.94 and 38.0 c.c. of **acetylene**. G. P. Schweder noted that when heated with **carbon**, at not too high a temp., cobalt sulphate is reduced to cobalt sulphide. J. H. Weibel studied the action of **carbon monoxide**. C. A. L. de Bruyn found that 100 parts of absolute **methyl alcohol** dissolve 1.04 parts of anhydrous cobalt sulphate at 18°; and 54.5 parts of the heptahydrate at 18°, and 42.8 parts at 3°; also 100 parts of 93.5 per cent. methyl alcohol dissolve 13.3 parts of the heptahydrate at 3°; and 100 parts of 50 per cent. methyl alcohol dissolve 1.8 parts of the heptahydrate at 3°. Again, 100 parts of absolute **ethyl alcohol** dissolve 2.5 parts of the heptahydrate at 3°. G. C. Gibson and co-workers found the solubilities in methyl and ethyl alcohols, *S* gram. of  $\text{CoSO}_4$  per 100 grms. of solvent, to be:

CH <sub>3</sub> OH					C <sub>2</sub> H <sub>5</sub> OH				
	15°	25°	45°	55°		15°	25°	45°	55°
<i>S</i>	0.300	0.418	0.373	0.267		0.017	0.018	0.023	0.026

F. W. O. de Coninck found that **ethylene glycol** dissolves 3 to 3.2 per cent. of cobalt sulphate, and A. Grün and F. Bockisch obtained a complex salt,  $\text{CoSO}_4 \cdot 3\text{C}_2\text{H}_6\text{O}_2 \cdot \text{H}_2\text{O}$ ; they also prepared a complex with **glycerol**, namely,  $\text{CoSO}_4 \cdot 3\text{C}_3\text{H}_5(\text{OH})_3 \cdot \text{H}_2\text{O}$ ; and with **glycerol- $\alpha$ -monomethylin**,  $\text{CoSO}_4 \cdot 2\text{C}_4\text{H}_{10}\text{O}_3$ . C. Dufraisse and D. Nakae studied the catalytic oxidation of **acetaldehyde**, **benzaldehyde**, **furfuraldehyde**, **styrene**, and **turpentine** in the presence of cobalt sulphate. J. Persoz observed that **acetic acid** precipitates cobalt sulphate from its aq. soln., and F. L. Cooper studied the absorption spectrum of soln. in conc. acetic acid. A. W. Davidson found that the anhydrous sulphate is insoluble in a soln. of **ammonium acetate**. A. Naumann found that the heptahydrate is insoluble in **ethyl acetate**, and in **benzonitrile**. S. Hakomori studied the action of **oxalic acid**, and of **citric acid**. F. W. O. de Coninck observed that **glycol** can dissolve 2.5 per cent. of cobalt sulphate. A. Werner and W. Spruck, J. Meyer and K. Gröhler, and W. Hieber and co-workers studied the complex salt with **ethylenediamine**,  $[\text{Co en}_3]\text{SO}_4$ ; J. Frejka and L. Zahlova, with **diaminobutane**; F. Calzolari, and

M. R. Menz, the complex salt with **hexamethylenetetramine**,  $\text{CoSO}_4 \cdot \text{C}_6\text{H}_{12}\text{N}_4 \cdot 9\text{H}_2\text{O}$ ; M. R. Menz, with **camphidine**; and A. Rosenheim and co-workers, with **thiocarbamide**,  $2\text{CoSO}_4 \cdot 3\text{CS}(\text{NH}_2)_2$ . Boiling **aniline** was found by A. L. Leeds to have no influence on the anhydrous sulphate, and S. Glasstone and co-workers, and D. Tombeck obtained a complex, with aniline, namely,  $\text{CoSO}_4 \cdot 4\text{C}_6\text{H}_5\text{NH}_2$ ; G. Spacu and R. Ripan, with **benzylamine**; J. Moitessier, and H. Schjerning, with **phenylhydrazine**; W. Hieber and co-workers, and R. Cernatescu and co-workers, with **phenylenediamine**; A. Smolka and A. Friedrich, with **phenylguanidine**; E. Thilo and H. Heilborn, with **diacetyldioxime**,  $[\text{Co}(\text{CH}_3\text{CNOH})_2]\text{SO}_4$ ; F. Reitzenstein, F. Schlegel, R. F. Weinland and K. Effinger, A. Hantzsch, and G. Spacu and co-workers, with **pyridine**; G. Canneri, with **guanidine**; F. L. Hahn and co-workers, with  $\alpha$ -**acetaminopyridine**; E. Borsbach, and F. Reitzenstein, with **quinoline**; P. C. and N. Ray, with **ethylsulphonium sulphate**,  $\text{CoSO}_4 \cdot \{(\text{C}_2\text{H}_5)_3\text{S}\}_2 \cdot \text{SO}_4 \cdot 10\text{H}_2\text{O}$ ; W. Hieber and co-workers, with **trihydroxyethylamine**; K. A. Jensen and E. R. Madsen, with **thiosemicarbazide**; and A. Tettamanzi and B. Carli, with **triethanolamine**. A. V. Pavlinova studied the oxidation of ammoniacal solutions of **potassium ferrocyanide** in the presence of cobalt sulphate as catalyst.

G. Gore discussed the adsorption of cobalt sulphate from its aq. soln. by **silica**. R. Kremann and co-workers found that **zinc** or **cadmium** will precipitate cobalt from soln. of its sulphate; and that at room temp. the precipitate contains metal and hydroxide—the proportion of hydroxide decreases with a rise of temp., and increases with the ratio of the zinc or cadmium to the precipitated cobalt. T. Heymann and K. Jellinek studied the equilibrium with **nickel**:  $\text{Ni} + \text{Co} \rightleftharpoons \text{Co} + \text{Ni}$ , and R. Schenck and E. Raub represented the reaction with **cobalt**:  $\text{CoSO}_4 + 4\text{Co} = 4\text{CoO} + \text{CoS}$ . E. J. Mills and J. J. Smith studied the mutual precipitation of cobalt and nickel by hydroxides by adding **alkali-lye** to aq. soln. of their sulphates—*vide supra*, basic salts. G. Vortmann found that boiling alkali-lye has very little action on the monohydrated sulphate. J. A. Hedvall, and J. A. Hedvall and J. Heuberger found that moist strontium oxide begins to react with the anhydrous sulphate at  $2^\circ$  to  $30^\circ$ ; and the dry oxide, at  $60^\circ$ . The reaction with **baryta** begins at  $328^\circ$ ; with **strontia**, at  $431^\circ$ ; with **lime**, at  $533^\circ$ ; and with **magnesia**, at  $592^\circ$ . D. Balareff and B. Srebrow studied the reaction with baryta. R. Schenck and E. Raub studied the action of the sulphate on **cobalt sulphide** (*q.v.*); and O. Ruff and B. Hersch, the action of **ferrous sulphide**, and of **nickel hydroxide**. W. Meigen found that aq. soln. of cobalt sulphate, colour **calcite** blue; and **aragonite**, lilac. D. Längauer studied the system:  $\text{CoSO}_4 + 2\text{KCl} \rightleftharpoons \text{CoCl}_2 + \text{K}_2\text{SO}_4$ . J. L. Proust discussed the sympathetic ink (*q.v.*) made with a soln. of cobalt sulphate.

**The double salts of cobalt sulphate.**—J. L. Proust,<sup>2</sup> and E. Mitscherlich prepared **ammonium cobaltous disulphate**,  $(\text{NH}_4)_2\text{Co}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , by crystallization from a soln. of the component salts. A. and H. Benrath's study of the system:  $\text{CoSO}_4 - (\text{NH}_4)_2\text{SO}_4 - \text{H}_2\text{O}$ , is summarized in Fig. 121. The region of the 1:1:6 double salt is stippled, and  $\text{Co}_1$ ,  $\text{Co}_2$ , and  $\text{Co}_3$  refer, respectively, to the mono-, hexa-, and hepta-hydrates of cobalt sulphate. R. M. Caven and W. K. Gardner's observations on the ternary system, at  $25^\circ$ , are summarized in Fig. 122. The ruby-red crystals of the double salt are either short prisms, or more or less tabular; they were found by J. C. G. de Marignac to be monoclinic, with the axial ratios  $a:b:c = 0.7392:1:0.4985$ , and  $\beta = 106^\circ 56'$ ; A. E. H. Tutton gave  $0.7386:1:0.4975$ , and  $\beta = 107^\circ 2'$ . The crystals were also examined by J. Grailich and V. von Lang, and W. Hofmann. The optic axial angles observed by A. Murmann and L. Rotter were  $2E = 155^\circ 12'$ , and  $2V_a = 81^\circ 39'$ . A. E. H. Tutton gave:

	Li-	C-	Na-	Tl-	Cd-	F-light
$2E$ . . .	$156^\circ 17'$	$156^\circ 35'$	$158^\circ 38'$	$160^\circ 47'$	—	—
$2H_a$ . . .	$72^\circ 38'$	$72^\circ 36'$	$72^\circ 26'$	$72^\circ 16'$	$72^\circ 30'$	$72^\circ 3'$
$2H_o$ . . .	$85^\circ 50'$	$85^\circ 46'$	$85^\circ 20'$	$84^\circ 54'$	$84^\circ 39'$	$84^\circ 20'$
$2V_a$ . . .	$82^\circ 1'$	$82^\circ 2'$	$82^\circ 9'$	$82^\circ 17'$	$82^\circ 21'$	$82^\circ 27'$

The value of  $2E$  for Na-light is  $153^\circ 5'$  at  $70^\circ$ , corresponding with a decrease in the optic axial angle to the extent of  $5.5^\circ$  for a rise of temp. of  $55^\circ$ . F. Halla and E. Mehl examined the X-radiograms, and obtained for the parameters  $a=9.23$  A.,  $b=12.49$  A., and  $c=6.23$  A., and  $B=106^\circ 56'$ , and the elementary cell contains 2 mols. The pleochroism of the crystals was discussed by H. de Sénarmont, J. Müller, A. Murmann and L. Rotter, and C. Ehlers. H. Schiff gave 1.873 for the sp. gr.; F. L. Perrot, 1.88; O. Pettersson, 1.902 at  $18^\circ$ , and 1.907 at  $16.6^\circ$ ;

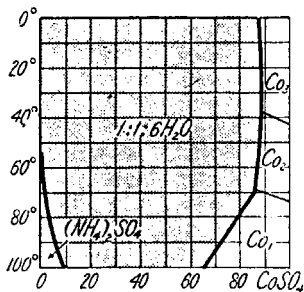


FIG. 121.—The Ternary System :  
( $\text{NH}_4$ ) $_2\text{SO}_4$ - $\text{CoSO}_4$ - $\text{H}_2\text{O}$ .

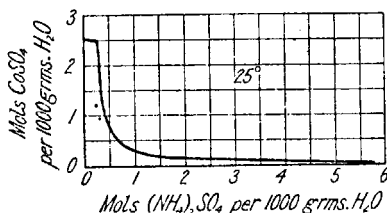


FIG. 122.—The Ternary System :  
( $\text{NH}_4$ ) $_2\text{SO}_4$ - $\text{CoSO}_4$ - $\text{H}_2\text{O}$ , at  $25^\circ$ .

H. Schröder, 1.893; R. Krickmeyer, 1.905 at  $18^\circ/4^\circ$ ; F. Halla and E. Mehl, 1.899 to 1.909 at  $25^\circ/4^\circ$ ; and A. E. H. Tutton, 1.901 at  $20^\circ/4^\circ$ , and for the mol. vol. 206.40. J. A. Groshaus, and O. Pettersson studied the mol. vol. and the contraction which attends the formation of the salt. B. Bertisch studied solid soln. of copper and cobalt ammonium sulphates. A. E. H. Tutton gave for the topic axial ratios, or the mol. distance ratios,  $\chi:\psi:\omega=6.1860:8.3753:4.1667$ . G. Quincke found the sp. gr. of a 12.64 per cent. soln. to be 1.1055. A. E. H. Tutton found that the salt, when heated, gives off water without melting. R. M. Caven and J. Ferguson found the vap. press.,  $p$  mm., of the hexahydrate to be :

	$35.3^\circ$	$43.8^\circ$	$50.7^\circ$	$61.7^\circ$	$67.3^\circ$	$82.2^\circ$
$p$	5.7	11.8	19.3	41.2	58.7	140.9

or  $\log p=7.600+3329T^{-1}-1,039,000T^{-2}$  as it passes to the dihydrate. The heat of hydration of the dihydrate is 74.8 Cals. per mol. of water vapour at  $50^\circ$ , and 1.03 Cals. per mol. of liquid water. E. Rouyer studied the mol. raising of the b.p. of aq. soln., and found indications of a marked dissociation of the double salt at  $100^\circ$ . C. Schaefer and M. Schubert observed maxima in the reflection at  $9.15\mu$ , and  $16.18\mu$ , and the first maximum when taken parallel to the  $a$ -axis, is at  $9.15\mu$ ; to the  $b$ -axis,  $9.21\mu$ ; and to the  $c$ -axis,  $8.83\mu$ . A. E. H. Tutton found the refractive indices to be, for :

	Li-	C-	Na-	Tl-	Cd-	F-	G-light
$\alpha$	1.4871	1.4876	1.4902	1.4930	1.4946	1.4964	1.5018
$\beta$	1.4922	1.4927	1.4953	1.4982	1.4998	1.5014	1.5067
$\gamma$	1.5001	1.5006	1.5032	1.5060	1.5076	1.5094	1.5148

The mean value for Na-light is 1.4962; and the double refraction,  $\gamma-\alpha=0.0130$ . E. Widmer gave 1.4962 for the mean value in the Na-light; and H. de Sénarmont, 1.492. A. Murmann and L. Rotter, for yellow-light,  $\alpha=1.489$ ,  $\beta=1.494$ , and  $\gamma=1.501$ ; and  $\beta=1.492$  for red-light, and 1.497 for green-light. A. E. H. Tutton gave  $\beta=1.4826+441,773\lambda^{-2}+449,400,000,000\lambda^{-4}+\dots$ . The index  $\alpha$  is reproduced if the constant 1.4826 is reduced by 0.0051; and the index  $\gamma$ , if the constant 1.4826 is increased by 0.0079. Observations at  $70^\circ$  show that the values of  $\alpha$  are diminished by about 0.0020, and the values of  $\gamma$  by about 0.0025 for  $55^\circ$  rise of temp. The sp. refractions for the  $\mu^2$ -formula for the  $C(H_a)$  and  $H_\gamma$  (near  $G$ )-rays are, respectively,  $\alpha=0.1515$ , and 0.1552;  $\beta=0.1528$ , and 0.1565; and  $\gamma=0.1549$ ,



and 0.1586; the corresponding mol. refractions are  $\alpha=59.43$ , and  $60.89$ ;  $\beta=59.95$  and  $62.22$ ; and  $\gamma=60.77$ , and  $62.22$ ; or with the  $\mu$ -formula and the  $C$ -ray,  $\alpha=100.64$ ,  $\beta=101.70$ , and  $\gamma=103.33$ -mean  $101.89$ ; the sp. dispersions for the  $\mu^2$ -formula and the  $G$ - and  $C$ -rays are  $\alpha=\beta=\gamma=0.0037$ ; and the mol. dispersions  $\alpha=1.46$ , and  $\beta=\lambda=1.45$ . C. Ehlers discussed the absorption spectrum of the solid; and W. W. Coblentz, the absorption spectrum of the soln.; L. R. Ingersoll, and R. W. Roberts studied the magnetic rotation of the plane of polarization; and W. L. Goodwin, the feeble transparency for X-rays. Observations on the magnetic susceptibility were made by G. Wiedemann, and N. S. Krishnan and co-workers. W. Finke gave for the susceptibilities of the hexahydrate in the three axial directions,  $a$ ,  $b$ , and  $c$ , respectively,  $55.95 \times 10^{-6}$ ,  $43.55 \times 10^{-6}$ , and  $45.50 \times 10^{-6}$  vol. unit. H. Moehle found the magnetic susceptibility to be  $3.84 \times 10^{-6}$  mass unit. I. I. Rabi observed with the three planes of symmetry at  $27^\circ$ ,  $\chi_1=29.6 \times 10^{-6}$ ,  $\chi_2=21.4 \times 10^{-6}$ , and  $\chi_3=25.7 \times 10^{-6}$  mass unit; and L. C. Jackson, at  $17.8^\circ$ ,  $-232.7^\circ$ , and  $258.22^\circ$ , respectively,  $\chi \times 10^6=24.61$ ,  $241.2$ , and  $321.6$  mass unit—see Fig. 119. Observations were also made by L. C. Jackson and H. K. Onnes. The magneton numbers were also discussed by L. C. Jackson, L. Pauling and M. L. Huggins, and L. C. Jackson and H. K. Onnes. According to G. Quincke, the magnetic susceptibility of an aq. soln. of the salt is  $37.2 \times 10^{-6}$  mass unit at  $18^\circ$  to  $20^\circ$ . Observations were also made by H. Moehle, and B. W. Bartlett. H. E. Armstrong and E. H. Rodd studied the crystallization in a magnetic field. C. von Hauer found that at  $20^\circ$ , a sat. soln. has  $14.9$ ; at  $40^\circ$ ,  $20.8$ ; at  $60^\circ$ ,  $25.6$ ; and at  $80^\circ$ ,  $33.0$  per cent. of the anhydrous salt; J. Locke observed that at  $25^\circ$ , a litre of water can dissolve  $147.2$  grms. of the anhydrous salt; and E. Tobler found the solubility,  $S$  grms. of anhydrous salt per 100 grms. of water, to be:

	0°	10°	18°	23°	35°	40°	45°	50°	60°	75°
$S$	8.9	11.6	15.2	17.1	19.6	22.3	25.0	28.7	34.5	43.3

Observations on the solubility were also made by B. Bertisch, and H. T. Kalmus and co-workers. A. Watt described the use of the salt for the electrodeposition of cobalt. S. Miyamoto studied the reduction of the salt by hydrogen in the silent discharge. E. Alberts studied the action of carbon dioxide. G. Spacu and R. Ripan prepared a complex with benzylamine, namely,  $[\text{Co}(\text{NH}_2\text{CH}_2.\text{C}_6\text{H}_5)_2(\text{H}_2\text{O})_2](\text{NH}_4\text{SO}_4)_2$ ; and with pyridine,  $[\text{Co py}_2(\text{H}_2\text{O})_4](\text{NH}_4\text{SO}_4)_2$ .

C. Lepierre and M. Lachaud prepared **ammonium cobalt pentasulphate**,  $2(\text{NH}_4)_2\text{SO}_4.3\text{CoSO}_4$ , by fusing anhydrous cobalt sulphate, or the oxide, hydroxide, or carbonate, with 5 or 6 times its weight of ammonium hydrosulphate. The carmine-red, octahedral, cubic crystals can be rapidly washed with cold water and alcohol. The crystals become hydrated in contact with water. If the salt is heated with ammonium sulphate, it furnishes octahedral crystals of anhydrous cobalt sulphate.

T. Curtius and F. Schrader obtained **hydrazine cobaltous disulphate**,  $(\text{N}_2\text{H}_5)_2\text{Co}(\text{SO}_4)_2$ , in rose-red, microscopic crystals, by mixing conc. soln. of hydrazine and cobalt sulphates. One part of the salt dissolves in 305.16 parts of water at  $12^\circ$ . When the red, ammoniacal soln. is boiled, it furnishes a red precipitate of  $\text{CoSO}_4.3\text{N}_2\text{H}_4.\text{H}_2\text{O}$ . The salt is oxidized by nitric acid, and it is insoluble in hydrochloric acid.

J. L. Proust, and E. Mitscherlich prepared **potassium cobaltous disulphate**,  $\text{K}_2\text{Co}(\text{SO}_4)_2.6\text{H}_2\text{O}$ , from a mixed soln. of the component salts. The red crystals of the *hexahydrate* resemble those of the corresponding potassium magnesium disulphate. F. R. Mallet prepared carmine-red, tetrahedral crystals of the anhydrous salt by fusing a mixture of the component sulphates in theoretical proportions. C. von Hauer obtained very well-developed crystals in the presence of some zinc sulphate. The salt rapidly forms the hexahydrate on exposure to air. O. Aschan, O. Aschan and G. V. Petrelius, and H. Marshall obtained it by the action of a soln. of potassium persulphate on cobalt sulphate. A. Ploin studied solid

soln. of copper and cobalt potassium sulphates. G. Calcagni and D. Marotta studied the f.p. curves of the binary system:  $\text{K}_2\text{SO}_4\text{--CoSO}_4$ , and the results are summarized in Fig. 123. The compound  $\text{K}_2\text{SO}_4\cdot\text{CoSO}_4$  is formed, and decomposes at  $560^\circ$ ; and there is also formed **potassium cobaltous trisulphate**,  $\text{K}_2\text{SO}_4\cdot 2\text{CoSO}_4$ , which crystallizes at  $736^\circ$ , and has a eutectic at about  $725^\circ$  with 31 per cent.  $\text{K}_2\text{SO}_4$ . At  $735^\circ$  there is a eutectic corresponding with 60 per cent.  $\text{K}_2\text{SO}_4$ . There is no sign of the **potassium cobaltous pentasulphate**,  $3\text{K}_2\text{SO}_4\cdot 2\text{CoSO}_4$ , reported by S. P. Sadtler to be formed in crystals with a definite m.p., when the component salts are fused together in theoretical proportions. This salt was also examined by O. W. Gibbs and F. A. Gent, and A. A. Julien. R. M. Caven and W. Johnston examined the ternary system:  $\text{CoSO}_4\text{--K}_2\text{SO}_4\text{--H}_2\text{O}$ , at  $25^\circ$ , and expressing the concentrations of sat. soln. in mols of salt per 1000 grms. of water, they obtained the following results (plotted in Fig. 124):

$\text{CoSO}_4$	0	0.150	0.239	0.458	1.095	2.205	2.557	2.536	2.433
$\text{K}_2\text{SO}_4$	0.680	0.737	0.780	0.531	0.361	0.240	0.212	0.190	0
	$\text{K}_2\text{SO}_4$			$\text{K}_2\text{Co}(\text{SO}_4)_2\cdot 6\text{H}_2\text{O}$			$\text{CoSO}_4\cdot 7\text{H}_2\text{O}$		

A. and H. Benrath's study of the ternary system is summarized in Fig. 125. The region of the 1:1:6 double salt is stippled.  $\text{Co}_1$ ,  $\text{Co}_6$ , and  $\text{Co}_7$ , respectively, denote the mono-, hexa-, and hepta-hydrates of cobalt sulphate. Observations on the crystals were made by E. Mitscherlich, W. Hofmann, and J. Grailich and

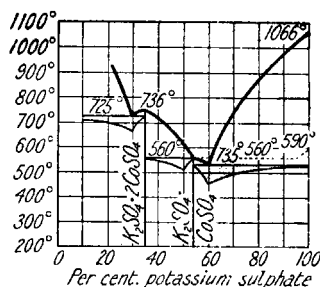


FIG. 123.—The Freezing-point Curves of the System:  $\text{K}_2\text{SO}_4\text{--CoSO}_4$ .

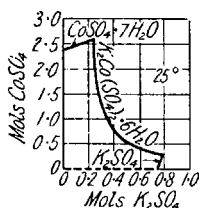


FIG. 124.—The System:  $\text{K}_2\text{SO}_4\text{--CoSO}_4\text{--H}_2\text{O}$ , at  $25^\circ$ .

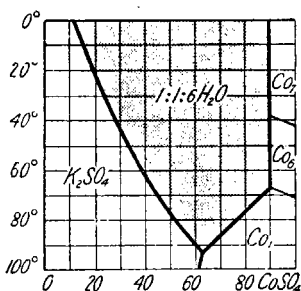


FIG. 125.—The Ternary System:  $\text{K}_2\text{SO}_4\text{--CoSO}_4\text{--H}_2\text{O}$ .

V. von Lang, C. Montemartini and L. Losana studied the quaternary system:  $\text{CoSO}_4\text{--K}_2\text{SO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$ , at temp. between  $0^\circ$  and  $25^\circ$ . The solid phases were  $\text{CoSO}_4$ ,  $\text{CoSO}_4\cdot 6\text{H}_2\text{O}$ ,  $\text{CoSO}_4\cdot 2\text{H}_2\text{O}$ ,  $\text{CoSO}_4\cdot \text{H}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4\cdot \text{CoSO}_4\cdot 6\text{H}_2\text{O}$ ,  $\text{KHSO}_4\cdot \text{H}_2\text{O}$ ,  $\text{KHSO}_4\cdot \text{H}_2\text{SO}_4$ , and  $\text{K}_2\text{SO}_4\cdot \text{KHSO}_4\cdot \text{H}_2\text{O}$ .

According to A. E. H. Tutton, the crystals of the hexahydrate,  $\text{K}_2\text{Co}(\text{SO}_4)_2\cdot 6\text{H}_2\text{O}$ , are prismatic or tabular, monoclinic crystals with the axial ratios  $a:b:c = 0.7404:1:0.5037$ , and  $\beta = 104^\circ 55'$ . A. Murmann and L. Rotter gave  $0.7327:1:0.4705$ , and  $\beta = 105^\circ 7'$ . There is a cleavage parallel to the  $(\bar{2}01)$ -face. The optic axial angles, measured by A. E. H. Tutton, are:

	Li-	C-	Na-	Tl-	F-light
$2E$	$113^\circ 56'$	$114^\circ 0'$	$114^\circ 25'$	$114^\circ 56'$	$115^\circ 40'$
$2H_a$	$61^\circ 4'$	$61^\circ 2'$	$60^\circ 51'$	$60^\circ 40'$	$60^\circ 12'$
$2H_o$	$96^\circ 13'$	$96^\circ 5'$	$95^\circ 40'$	$95^\circ 11'$	$94^\circ 35'$
$2V$	$68^\circ 38'$	$68^\circ 29'$	$68^\circ 41'$	$68^\circ 44'$	$68^\circ 48'$

A rise of temp. increased  $2E$  about  $2^\circ 15'$  for  $50^\circ$  rise of temp. Observations on the crystals were also made by H. Töpsöe and C. Christiansen; and the formation of solid soln. with the corresponding  $K_2SO_4 \cdot CuSO_4 \cdot 6H_2O$ , by A. Plöin. H. Schröder gave 3.105 for the sp. gr. of the anhydrous salt; and for the hexahydrate, H. Schiff gave 2.154; R. Krickmeyer, 2.218 at  $20^\circ/4^\circ$ ; O. Pettersson, 2.205 at  $16.8^\circ$ , and 2.214 at  $16.6^\circ$ ; and A. E. H. Tutton, 2.219 at  $20^\circ/4^\circ$ , 195.68 for the mol. vol., and for the mol. distance ratios, *i.e.* the topic axial angles,  $\chi : \psi : \omega = 6.0405 : 8.1583 : 4.1093$ . The subject was discussed by J. A. Groshaus. The mol. vol., and the contraction which occurs in the formation of the salt were discussed by F. Ephraim and co-workers, P. Niggli, and O. Pettersson. G. Tammann measured the rate of diffusion of the salt. R. M. Caven and J. Ferguson found the vap. press.,  $p$  mm., for the hexahydrate to be :

	$26.5^\circ$	$39.6^\circ$	$45.7^\circ$	$51.1^\circ$	$57.0^\circ$	$66.6^\circ$	$66.3^\circ$	$70.3^\circ$
$p$ . . .	7.2	19.2	30.6	44.2	64.2	81.6	114.6	201.3

or  $\log p = 6.764 - 265.77T^{-1} - 451,350T^{-2}$  for the passage to the dihydrate. The heat of hydration of the dihydrate is 14.0 Cals. per mol of water vapour. R. M. Caven and J. Ferguson gave for the heat of hydration, 520 cals. of liquid water, and at  $50^\circ$ , 14 cals. per mol of water vapour. A. E. H. Tutton gave for the refractive indices of the hexahydrate :

	Li-	C-	Na-	Tl-	F-	G-light
$\alpha$ . . .	1.4780	1.4784	1.4807	1.4830	1.4861	1.4904
$\beta$ . . .	1.4838	1.4842	1.4865	1.4889	1.4919	1.4961
$\gamma$ . . .	1.4973	1.4977	1.5004	1.5028	1.5059	1.5105

The mean value for Na-light is 1.4892, and the double refraction  $\gamma - \alpha = 0.0197$ . H. de Sénarmont gave for the refractive index, 1.465; and C. Schaefer and M. Schubert, for the  $D$ -line,  $\alpha = 1.4807$ ,  $\beta = 1.4867$ , and  $\gamma = 1.5004$ ; and A. Murmann and L. Rotter gave  $\beta = 1.482$  for red-light, 1.487 for yellow-light, and 1.490 for green-light. A. E. H. Tutton represented his results by  $\beta = 1.4737 + 514824\lambda^{-2} + 1,962,700,000,000\lambda^{-4} + \dots$ ; and for  $\alpha$ , the constant 1.4737 is diminished by 0.0058, and for  $\gamma$ , the constant is increased by 0.0138. The indices of refraction are lowered by about 0.0020 for  $50^\circ$  rise of temp. The optical character is positive. The sp. refractions with the  $\mu^2$ -formula, for the  $C$ - and  $G$ -rays, are, respectively,  $\alpha = 0.1282$ , and 0.1309;  $\beta = 0.1295$ , and 0.1322; and  $\gamma = 0.1325$ , and 0.1354; the mol. refractions,  $\alpha = 56.08$ , and 57.28;  $\beta = 56.66$ , and 57.84; and  $\gamma = 58.00$ , and 59.26; the mol refraction for the  $C$ -line with the  $\gamma$ -formula are  $\alpha = 94.72$ ,  $\beta = 95.87$ , and  $\gamma = 98.54$ ; the sp. dispersions for the  $G$ - and  $C$ -rays for the  $\mu^2$ -formula are  $\alpha = \beta = 0.0027$ , and  $\gamma = 0.0029$ ; and the mol. dispersions  $\alpha = 1.20$ ,  $\beta = 1.18$ , and  $\gamma = 1.26$ . These values are nearly constant for all temp. at which the crystals are stable, because refraction and sp. gr. vary with temp. in the same direction. C. Schaefer and M. Schubert found maxima in the reflection to occur in the ultra-red at  $9.03\mu$  and  $15.90\mu$ ; and the first maxima in the directions of the three axes are  $a$  at  $9.10\mu$ ;  $b$  at  $8.89\mu$ ; and  $c$  at  $8.76\mu$ . The mol. refractions were discussed by W. J. Pope, E. Widmer, and C. Ehlers; the absorption spectrum, by C. Ehlers; the slight transparency for X-rays, by W. L. Goodwin, and the feeble triboluminescence, by A. Imhof. H. Moehle found the mass susceptibility to be  $3.448 \times 10^{-6}$  vol. unit; and W. Finke gave for the three axial directions,  $a$ ,  $b$ , and  $c$ , respectively,  $66.59 \times 10^{-6}$ ,  $49.62 \times 10^{-6}$ , and  $77.15 \times 10^{-6}$  vol. unit. I. I. Rabi found for the three planes of symmetry,  $\chi_1 = 25.9 \times 10^{-6}$ ,  $\chi_2 = 20.1 \times 10^{-6}$ , and  $\chi_3 = 21.9 \times 10^{-6}$  mass unit; and L. C. Jackson, and L. C. Jackson and H. K. Onnes gave, respectively,  $\chi_1 \times 10^6$ ,  $\chi_2 \times 10^6$ , and  $\chi_3 \times 10^6$ , at  $17^\circ$ ,  $28.4^\circ$ ,  $23.0^\circ$ , and  $24.6^\circ$  mass unit; at  $-43^\circ$ ,  $37.0^\circ$ ,  $27.0^\circ$ , and  $30.1^\circ$  mass unit; and at  $-103^\circ$ ,  $52.7^\circ$ ,  $32.8^\circ$ , and  $38.8^\circ$  mass unit. Observations were also made by B. W. Bartlett, and N. S. Krishnan and co-workers. The magneton numbers were discussed by B. Cabrera, and L. C. Jackson and H. K. Onnes. H. Baubigny and E. Péchard found that the rate of efflorescence of the crystals in dry air is considerably increased if

the salt is deposited from slightly acidic soln. J. L. Proust noted that the salt is less soluble in water than is cobalt sulphate. C. von Hauer found that a sat. soln. at 20° has 14; at 40°, 19.5; at 60°, 24.4; and at 80°, 31.8 per cent. of anhydrous salt; J. Locke, that a litre of water at 25° dissolves 128.8 grms. of anhydrous salt; and E. Tobler found that the solubility, *S* grms. of the anhydrous salt in 100 grms. of water, is:

	0°	12°	15°	20°	25°	30°	35°	40°	49°
<i>S</i>	19.1	30	32.5	34.9	45.3	51.9	55.4	64.6	81.3

Observations were made by G. J. Mulder, and R. M. Caven and W. Johnston (Fig. 124). R. M. Caven and J. Ferguson observed a dihydrate is formed at 80°, and the anhydrous salt at 95°. G. Spacu prepared complex salts with pyridine, namely,  $K_2Co(SO_4)_2 \cdot 3C_5H_5N \cdot 3H_2O$ , and  $K_2Co(SO_4)_2 \cdot 2C_5H_5N \cdot 4H_2O$ . The results of D. Längauer's study on the reciprocal pairs of salts:  $CoSO_4 + K_2Cl_2 \rightleftharpoons CoCl_2 + K_2SO_4$ , are summarized in Fig. 126.

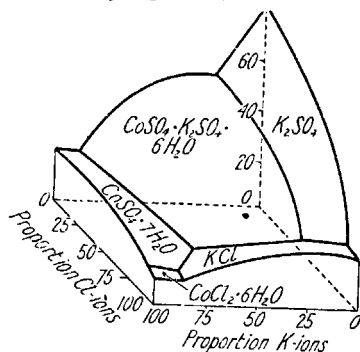


FIG. 126.—Solid Phases in the Reaction:  $CoSO_4 + K_2Cl_2 \rightleftharpoons CoCl_2 + K_2SO_4$ .

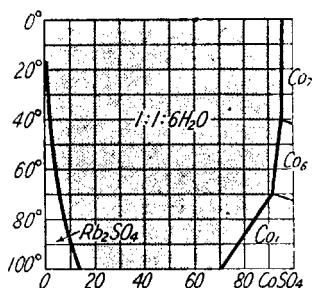


FIG. 127.—The Ternary System:  $Rb_2SO_4 - CoSO_4 - H_2O$ .

R. Bunsen and G. Kirchhoff prepared **rubidium cobaltous disulphate**,  $Rb_2Co(SO_4)_2 \cdot 6H_2O$ , from a soln. of the component salts. F. R. Mallet obtained crystals of the anhydrous salt by fusing a mixture of the theoretical proportions of the component salts. A. and H. Benrath's study of the system:  $Rb_2SO_4 - CoSO_4 - H_2O$ , is summarized in Fig. 127. The region of the 1 : 1 : 6 double salt is stippled,  $Co_1$ ,  $Co_6$ , and  $Co_7$ , respectively, refer to the mono-, hexa-, and hepta-hydrates of cobalt sulphate. The ruby-red or reddish-brown crystals of the *hexahydrate* are usually tabular or prismatic, and belong to the monoclinic system having the axial ratios  $a : b : c = 0.7391 : 1 : 0.5011$ , and  $\beta = 106^\circ 1'$ . F. L. Perrot gave  $0.738986 : 1 : 0.494805$ , and  $\beta = 106^\circ 2' 25''$ . A. E. H. Tutton observed that the cleavage parallel to the (201)-face is well developed. The crystals are isomorphous with those of the corresponding magnesium, zinc, cadmium, manganous, and nickel salts. The optic axial angles are:

	Li-	C-	Na-	Tl-	F-light
$2E$	129° 46'	129° 51'	130° 10'	130° 29'	130° 55'
$2H_a$	66° 37'	66° 34'	66° 19'	66° 1'	54° 37'
$2H_o$	90° 53'	90° 49'	90° 33'	90° 12'	89° 44'
$2V_a$	75° 15'	75° 14'	75° 11'	75° 8'	75° 3'

The optical axial angle  $2E$  increases about  $2^\circ$  for every  $50^\circ$  rise of temp. F. L. Perrot gave 2.56 for the sp. gr., and A. E. H. Tutton, 2.567 at  $20^\circ/4^\circ$ , and mol. vol. 205.03. The mol. distance ratios, i.e. the topic axial ratios,  $\chi : \psi : \omega = 6.1494 : 8.3201 : 4.1692$ . The mol. vol. and the vol. contraction were studied by F. Ephraim and co-workers, and P. Niggli. R. M. Caven and C. J. Ferguson found the vap. press., *p* mm., of the hexahydrate to be:

	28.4°	33.3°	38.4°	45.3°	52.6°	58.9°	65.1°	76.1°
<i>p</i>	4.3	6.8	9.7	16.3	26.9	41.7	59.9	112.2

or  $\log p = 3.740 + 1594T^{-1} - 762,740T^{-2}$  for the passage to the dihydrate. The heat of hydration of the dihydrate is 14.3 Cals. per mol of water vapour. According to A. E. H. Tutton, the refractive indices are :

	Li-	C-	Na-	Tl-	F-	G-light
$\alpha$ . . .	1.4833	1.4837	1.4859	1.4882	1.4910	1.4954
$\beta$ . . .	1.4889	1.4893	1.4916	1.4940	1.4968	1.5011
$\gamma$ . . .	1.4985	1.4989	1.5014	1.5038	1.5068	1.5114

The mean value for Na-light is 1.4962, and the double refraction  $\gamma - \alpha = 0.0130$ . The optical character is positive. Observations were made by F. L. Perrot, and W. J. Pope. F. L. Perrot gave  $\alpha = 1.50123$ ,  $\beta = 1.49165$ , and  $\gamma = 1.48596$  for the *D*-line. A. E. H. Tutton found that the index  $\beta = 1.4789 + 507,763\lambda^{-2} + 1,841,600,000,000\lambda^{-4} + \dots$ . The  $\alpha$  indices can be represented by this formula if 1.4789 be lowered by 0.0057; and the  $\gamma$  indices if the constant 1.4789 be raised by 0.0098. The refractive indices are lowered by about 0.0016 for 50° rise of temp. The sp. refractions with the  $\mu^{-2}$ -formula for the *C*- and *G*-rays are, respectively,  $\alpha = 0.1119$ , and 0.1142;  $\beta = 0.1130$ , and 0.1153; and  $\gamma = 0.1149$ , and 0.1173; and the mol. refractions,  $\alpha = 59.31$ , and 60.53,  $\beta = 59.90$ , and 61.12, and  $\gamma = 60.89$ , and 62.18. The corresponding sp. dispersions for the *G*- and *C*-rays are  $\alpha = \beta = 0.0023$ , and  $\gamma = 0.0024$ ; and the mol. dispersions,  $\alpha = \beta = 1.22$ , and  $\gamma = 1.29$ . The mol. refractions by the  $\mu$ -formula, and the *C*-line, are  $\alpha = 100.34$ ,  $\beta = 101.50$ , and  $\gamma = 103.49$ . A. A. Lutheroth studied the magnetic properties of the crystals. I. I. Rabi observed that for the three planes of symmetry, the magnetic susceptibility, at 27°, are  $\chi_1 = 22.0 \times 10^{-6}$ ,  $\chi_2 = 16.7 \times 10^{-6}$ , and  $\chi_3 = 19.1 \times 10^{-6}$  mass unit; and L. C. Jackson and H. K. Onnes found the values of  $\chi \times 10^6$  at 25°, -195.6°, and -258.34°, are, respectively, 20.98, 65.06, and 268.0 mass unit. The magneton numbers were discussed by B. Cabrera, and L. C. Jackson and H. K. Onnes. J. Locke found that a litre of water, at 25°, dissolves 92.8 grms. of the anhydrous salt. Observations were made by E. Biron.

R. Bunsen and G. Kirchhoff prepared **cæsium cobaltous disulphate**,  $\text{Cs}_2\text{Co}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , from a soln. of the component salts; and F. R. Mallet obtained crystals of the anhydrous salt by fusing a mixture of the theoretical proportions of the component salts. The brownish-red crystals of the *hexahydrate* are prismatic, and, according to A. E. H. Tutton, they belong to the monoclinic system, and have the axial ratios  $a : b : c = 0.7270 : 1 : 0.4968$ , and  $\beta = 107^\circ 8'$ . The cleavage parallel to the (201)-face is well developed. The optic axial angle  $2E$  is very large, for the Na-light the angle is probably near  $156^\circ 40'$ ; the other optic axial angles are, for :

	Li-	C-	Na-	Tl-	F-light
$2H_a$ . . .	$73^\circ 29'$	$73^\circ 12'$	$73^\circ 7'$	$72^\circ 48'$	$72^\circ 25'$
$2H_o$ . . .	$87^\circ 34'$	$87^\circ 30'$	$87^\circ 19'$	$87^\circ 9'$	$86^\circ 49'$
$2V_a$ . . .	$81^\circ 42'$	$81^\circ 40'$	$81^\circ 34'$	$81^\circ 29'$	$81^\circ 22'$

The sp. gr. is 2.844 at 20°/4°; the mol. vol., 218.11; and the mol. distance ratios, i.e. the topic axial ratios, are  $\chi : \psi : \omega = 6.2386 : 8.5814 : 4.2632$ . The mol. vol., and the vol. contraction were studied by F. Ephraim and co-workers, and P. Niggli. R. M. Caven and J. Ferguson found the vap. press.,  $p$  mm., of the hexahydrate to be :

	29.2°	41.0°	47.0°	53.8°	60.2°	75.0°
$p$ . . .	5.1	12.2	19.6	31.3	47.6	118.6

or  $\log p = 8.164 - 1221T^{-1} - 313,270T^{-2}$ , for the passage to the dihydrate. The heat of hydration of the dihydrate is 14.4 Cals. per mol. of water vapour. According to A. E. H. Tutton, the indices of refraction are :

	Li-	C-	Na-	Tl-	F-	G-light
$\alpha$ . . .	1.5028	1.5032	1.5037	1.5079	1.5112	1.5159
$\beta$ . . .	1.5057	1.5061	1.5085	1.5110	1.5142	1.5188
$\gamma$ . . .	1.5102	1.5106	1.5132	1.5156	1.5187	1.5237

The mean value for Na-light is 1.5091, and the double refraction  $\gamma - \alpha = 0.0075$ . The optical character is positive. The values for  $\beta$  can be represented by

$\beta=1.4952+532,337\lambda^{-2}+1,971,500,000,000\lambda^{-4}+\dots$ . The  $\alpha$  indices are closely reproduced if the constant 1.4952 is diminished by 0.0029, and the  $\gamma$  indices if that constant is increased by 0.0046. The refractive indices are lowered 0.0018 by a rise of temp. of 50°. The sp. refractions with the  $\mu^2$ -formula for the *C*- and *G*-rays are, respectively,  $\alpha=0.1043$ , and 0.1065;  $\beta=0.1048$ , and 0.1070; and  $\gamma=0.1056$ , and 0.1079; the mol. refractions,  $\alpha=65.19$ , and 66.57;  $\beta=65.51$ , and 66.89; and  $\gamma=66.00$ , and 67.41; the sp. dispersions,  $\alpha=\beta=0.0022$ , and  $\gamma=0.0023$ ; and the mol. dispersions,  $\alpha=\beta=1.38$ , and  $\gamma=1.41$ . The mol. refractions with the  $\mu$ -formula are  $\alpha=110.95$ ,  $\beta=111.58$ , and  $\gamma=112.57$ . Observations on the subject were made by W. J. Pope, and E. Widmer. J. Locke found that a litre of water at 25° dissolves 418.8 grms. of the anhydrous salt. The subject was studied by E. Biron.

C. F. Rammelsberg was unable to prepare **lithium cobaltous sulphate**; and G. Calcagni and D. Marotta observed no sign of such a compound on the f.p. curves of the binary system:  $\text{Li}_2\text{SO}_4\text{--CoSO}_4$ . There is a limited field of solid soln. from about 100 to 83 per cent. of  $\text{Li}_2\text{SO}_4$ , and there is a eutectic at  $595^\circ$  and 63 per

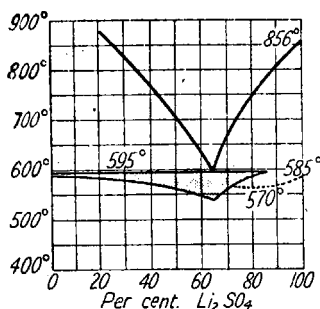
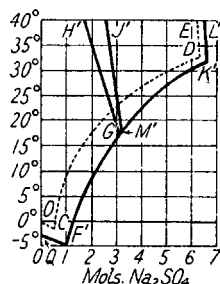
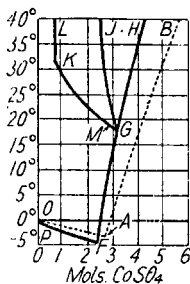


FIG. 128.—Freezing-point Curves of the System:  $\text{Li}_2\text{SO}_4\text{--CoSO}_4$ .



FIGS. 129 and 130.—Mutual Solubilities of Sodium and Cobaltous Sulphates.

cent.  $\text{Li}_2\text{SO}_4$ . J. Koppel and H. Wetzel, and H. Wetzel prepared pale red **sodium cobaltous disulphate**,  $\text{Na}_2\text{Co}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ , by melting together eq. proportions of the hydrated salts at  $25^\circ$ ; and their observations on the system:  $\text{Na}_2\text{SO}_4$ - $\text{CoSO}_4$ - $\text{H}_2\text{O}$  are summarized in Figs. 129 and 130. Corresponding soln. are designed with similar letters in both diagrams, those without the dash refer to cobalt sulphate, and those with the dash to sodium sulphate. The curves *FG* and *F'G'* refer to the solubilities of mixtures of the component sulphates; *GJ* and *G'J'*, to the solubility of the complex salt  $\text{Na}_2\text{Co}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ ; *GH* and *G'H'*, to that of a mixture of the complex salt and cobalt sulphate; *GKL* and *G'K'L'*, to that of a mixture of the complex salt and sodium sulphate; *OAB*, to the solubility of cobalt sulphate; *OCDE*, to the solubility of sodium sulphate; *A*, to the eutectic  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  and ice; and *C*, to the eutectic  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  and ice. The temp. of formation of the complex salt is  $17.5^\circ$ ; the transformation temp. of decahydrated sodium sulphate in the presence of cobalt sulphate, is  $31.5^\circ$ ; and the eutectic with a mixture of the two hydrated sulphates is  $-4.5^\circ$ . A. and H. Benrath examined the ternary system at  $97^\circ$ , and the following is a selection of their results for soln. in which the proportions of sodium and cobalt sulphates are expressed in percentages by weight; *x* denotes the mol. proportion of  $\text{CoSO}_4$  in the mixture, and *M*, the number of mols of water per mol. of salt:

CoSO <sub>4</sub>	0	4.80	6.38	9.21	24.07	28.13	28.91	31.21	34.33
Na <sub>2</sub> SO <sub>4</sub>	3.50	28.08	27.64	24.89	11.76	10.34	9.01	2.96	—
<i>x</i>	0	13.52	17.48	25.32	65.24	74.40	74.60	90.55	100.00
<i>M</i>	15.56	16.32	15.56	15.62	14.97	13.43	13.79	16.45	16.4

Na<sub>2</sub>SO<sub>4</sub>
Na<sub>2</sub>Co(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O
CoSO<sub>4</sub>·H<sub>2</sub>O

The results are plotted in Fig. 131; the dotted line refers to the sp. gr. of the soln. A. and H. Benrath's results at different temp. are summarized in Figs. 131 and 132. R. M. Caven and W. K. Gardner also studied the subject.

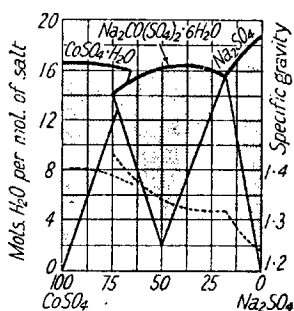


FIG. 131.—Equilibrium in the Ternary System:  $\text{Na}_2\text{SO}_4$ – $\text{CoSO}_4$ – $\text{H}_2\text{O}$ , at  $97^\circ$ .

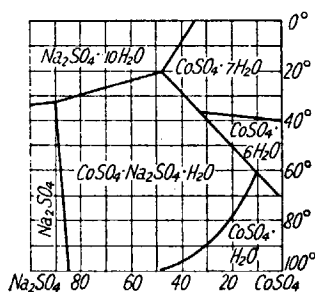


FIG. 132.—The Ternary System:  $\text{Na}_2\text{SO}_4$ – $\text{CoSO}_4$ – $\text{H}_2\text{O}$ .

O. Aschan reported the formation of crystals of **sodium cobalt disulphate**,  $\text{Na}_2\text{SO}_4\cdot\text{CoSO}_4\cdot 6\text{H}_2\text{O}$ , by the action of cobalt turnings on a soln. of sodium persulphate; and M. Wikul, of crystals of **sodium hydrodisulphate**,  $\text{NaHSO}_4\cdot(\text{CoO})_2\text{SO}_4\cdot 9\text{H}_2\text{O}$ , by the action of a soln. of cobalt nitrate and sodium sulphate in conc. sulphuric acid. The water of hydration is expelled at  $130^\circ$ . G. Calcagni and D. Marotta observed that fused mixtures of sodium and cobaltous sulphates form a compound **sodium cobaltous tetrasulphate**,  $3\text{Na}_2\text{SO}_4\cdot\text{CoSO}_4$ , Fig. 134, and it decomposes above  $425^\circ$ . Solid

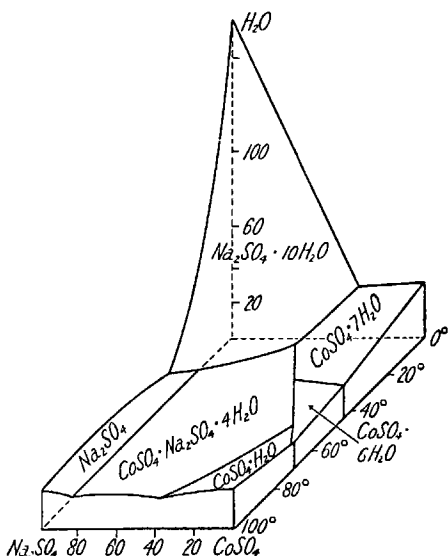


FIG. 133.—The Ternary System:  $\text{Na}_2\text{SO}_4$ – $\text{NiSO}_4$ – $\text{H}_2\text{O}$ .

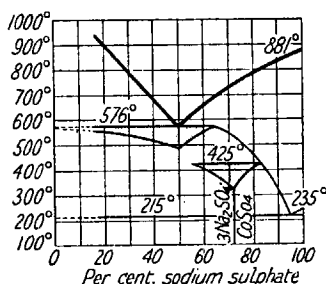


FIG. 134.—Freezing-point Curves of the Ternary System:  $\text{Na}_2\text{SO}_4$ – $\text{CoSO}_4$ .

soln. are formed when 100 to 67 per cent. of  $\text{Na}_2\text{SO}_4$  are present, and there is a eutectic at  $575^\circ$  when 50 per cent. of either component is present.

J. von Liebig described what he regarded as a **copper cobaltous sulphate**,  $\text{CuSO}_4\cdot 2\text{CoSO}_4\cdot 30\text{H}_2\text{O}$ , in monoclinic prisms resembling heptahydrated ferrous sulphate, dark green in reflected light, and rose-red in transmitted light. There was here an error in the determination of the water of crystallization, since C. von Hauer showed that the product is  $\text{CuSO}_4\cdot 2\text{CoSO}_4\cdot 21\text{H}_2\text{O}$ . He obtained this salt by the spontaneous evaporation of a soln. of cobalt sulphate in a sat. soln. of copper sulphate. The crystals are stable in air. A. Brezina showed that the crystals here are triclinic, like those of pentahydrated copper sulphate. A. Scott obtained crystals of the trihydrate,  $\text{CuSO}_4\cdot 2\text{CoSO}_4\cdot 3\text{H}_2\text{O}$ , in rose-red crystals, from a mixed

soln. of the component sulphate containing about 90 grms. of hydrated copper sulphate, 100 grms. of hydrated cobalt sulphate, 200 c.c. water, and then adding 130 c.c. of conc. sulphuric acid. It is probable that these products are solid soln. of copper and cobalt sulphates. E. Mitscherlich, A. Arzruni, E. Wohlwill, and J. W. Retgers observed that mixed soln. of the two salts furnish red, monoclinic crystals if the cobalt sulphate is in excess, and blue, triclinic crystals if the sulphate is in excess. H. D. Crockford and D. J. Brawley investigated the phases in the ternary system:  $\text{CuSO}_4\text{--CoSO}_4\text{--H}_2\text{O}$  at  $0^\circ$  and at  $25^\circ$ . The results at  $25^\circ$  are summarized in Fig. 135. The results at  $0^\circ$  and at  $25^\circ$  indicate the presence of pentahydrated copper sulphate, and of a series of solid soln. in which copper partially replaces cobalt in heptahydrated cobalt sulphate. The crystals of isomorphous mixtures or solid soln. of the two salts,  $(\text{Cu},\text{Co})\text{SO}_4\cdot 7\text{H}_2\text{O}$ , were measured by B. Bertisch, H. Dufet, A. Ploin, L. de Boisbaudran, and E. Jannettaz. According to G. Brügemann, when equal vols. of cold, sat. soln. of copper sulphate and cobalt chloride are mixed, and allowed to evaporate spontaneously, crystals containing sulphates of cobalt and copper were obtained, and chlorides of both metals remained in soln. W. Finke found the magnetic susceptibility of copper cobaltous sulphate,  $\text{CoSO}_4\cdot\text{CuSO}_4\cdot 6\text{H}_2\text{O}$ , to range from  $23.75 \times 10^{-6}$  to  $28.56 \times 10^{-6}$  mass unit. W. Finke

gave for the magnetic susceptibilities of  $\text{CoSO}_4 + \text{CuSO}_4 + 6\text{H}_2\text{O}$  in the three axial directions,  $a$ ,  $b$ , and  $c$ , respectively,  $28.62 \times 10^{-6}$ ,  $23.06 \times 10^{-6}$ , and  $25.57 \times 10^{-6}$  mass unit. A. Étard obtained rose-red crystals of **copper cobaltous hydrosulphate**,  $2\text{CuSO}_4\cdot 2\text{CoSO}_4\cdot \text{H}_2\text{SO}_4$ , by heating a sat. soln. of the constituent salts with a large excess of conc. sulphuric acid, in a sealed tube, at  $200^\circ$ . G. Spacu and R. Ripan reported a complex salt with benzylamine, namely,  $2\text{CoSO}_4\cdot \text{CuSO}_4\cdot 6\text{C}_6\text{H}_7(\text{NH}_2)\cdot 6\text{H}_2\text{O}$ ; and one with pyridine,  $2\text{CoSO}_4\cdot \text{CuSO}_4\cdot 7\text{C}_6\text{H}_5\text{N}\cdot 5\text{H}_2\text{O}$ . H. Vohl obtained violet-red crystals of **ammonium copper cobaltous sulphate**,  $2(\text{NH}_4)_2\text{SO}_4\cdot \text{CuSO}_4\cdot \text{CoSO}_4\cdot 12\text{H}_2\text{O}$ ; and likewise also **potassium copper cobaltous sulphate**,  $2\text{K}_2\text{SO}_4\cdot \text{CuSO}_4\cdot \text{CoSO}_4\cdot 12\text{H}_2\text{O}$ , but E. Aston and S. U. Pickering could not

establish the chemical individuality of these products, since they have the character of solid soln. A. Ploin studied the solid soln. of the potassium salt, and B. Bertisch, of the ammonium salt with the copper salt. A. Maible prepared **copper cobaltous trioxydisulphate**,  $2\text{CoSO}_4\cdot 3\text{CuO}\cdot 12\text{H}_2\text{O}$ , or, according to A. Werner,  $\text{Cu}_2(\text{OH})_4\text{Cu}=(\text{OH})_2\text{Co}(\text{SO}_4)_2\text{Co}\cdot 7\text{H}_2\text{O}$ , by the action of a cold soln. of 1 to 0.5 mol of  $\text{CoSO}_4$  per litre on  $4\text{CuO}\cdot \text{H}_2\text{O}$ . The salt is isomorphous with the corresponding salt of nickel. It occurs in chestnut-brown, hexagonal plates. If the soln. of copper sulphate has 0.25 mol per litre, crystals of **copper cobaltous dioxysulphate**,  $2\text{CuO}\cdot \text{CoSO}_4\cdot 6\text{H}_2\text{O}$ , are formed, and they are isomorphous with the corresponding nickel salt. W. A. Endriss made some observations on this subject. A. Recoura reported the basic salts,  $\text{CoSO}_4\cdot 3\text{CuO}\cdot n\text{H}_2\text{O}$ , to be formed by the action of a boiling, aq. soln. of cobalt sulphate on cupric hydroxide; and  $\text{CoSO}_4\cdot 24\text{CuO}\cdot n\text{H}_2\text{O}$ , from cupric hydroxide and a cold, aq. soln. of cobalt sulphate.

P. C. Ray and P. B. Sarkar, and P. B. Sarkar and N. Ray prepared **potassium cobaltous sulphatofluoberyllate**,  $\text{CoSO}_4\cdot \text{K}_2\text{BeF}_4\cdot 6\text{H}_2\text{O}$ , and **ammonium cobaltous sulphatofluoberyllate**,  $\text{CoSO}_4\cdot (\text{NH}_4)_2\text{BeF}_4\cdot 6\text{H}_2\text{O}$ , by crystallization from soln. of cobaltous sulphate and potassium or ammonium fluoberyllate.

G. C. Winkelblech obtained crystals of **magnesium cobaltous sulphate**,  $\text{MgSO}_4\cdot 3\text{CoSO}_4\cdot 28\text{H}_2\text{O}$ , from a soln. of the constituent salts; and H. Vohl reported **ammonium magnesium cobaltous sulphate**,  $2(\text{NH}_4)_2\text{SO}_4\cdot \text{MgSO}_4\cdot \text{CoSO}_4\cdot 12\text{H}_2\text{O}$ ;

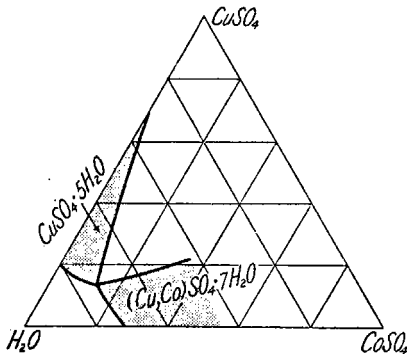


FIG. 135.—The Ternary System :  $\text{CuSO}_4\text{--CoSO}_4\text{--H}_2\text{O}$ , at  $25^\circ$ .



and **potassium magnesium cobaltous sulphate**,  $2\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot \text{CoSO}_4 \cdot 12\text{H}_2\text{O}$ , to be formed from soln. of the component salts, but E. Aston and S. U. Pickering could not establish the chemical individuality of these products, and they regarded them as solid soln. G. Spacu and R. Ripan reported complex salts with benzylamine,  $2\text{CoSO}_4 \cdot \text{MgSO}_4 \cdot 5\text{C}_7\text{H}_7(\text{NH}_2) \cdot 7\text{H}_2\text{O}$ ; and with pyridine,  $2\text{CoSO}_4 \cdot \text{MgSO}_4 \cdot 7\text{C}_5\text{H}_5\text{N} \cdot 5\text{H}_2\text{O}$ . D. Link reported that mixed soln. of cobalt and zinc sulphates furnished red, four-sided prisms of **zinc cobaltous sulphate**, which, on exposure to air, crumble to a white powder. H. Bassett and I. Sanderson examined the cadmium-cobaltous-sulphate system at  $25^\circ$  and  $80^\circ$ , but no definite compound of the two sulphates was observed. S. Meyer studied the crystallization of the salt in a magnetic field. H. Vohl reported **ammonium zinc cobaltous sulphate**,  $2(\text{NH}_4)_2\text{SO}_4 \cdot \text{ZnSO}_4 \cdot \text{CoSO}_4 \cdot 12\text{H}_2\text{O}$ , and **potassium zinc cobaltous sulphate**,  $2\text{K}_2\text{SO}_4 \cdot \text{ZnSO}_4 \cdot \text{CoSO}_4 \cdot 12\text{H}_2\text{O}$ , from soln. of the component salts. It is probable that these products are solid soln.

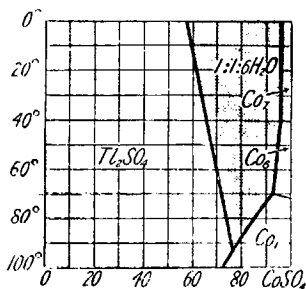


FIG. 136.—The Ternary System:  $\text{Ti}_2\text{SO}_4\text{--CoSO}_4\text{--H}_2\text{O}$ .

O. Pettersson prepared ruby-red, prismatic crystals of **thallous cobaltous disulphate**,  $\text{Ti}_2\text{Co}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , from a mixed soln. of the component salts. The system  $\text{CoSO}_4\text{--Ti}_2\text{SO}_4\text{--H}_2\text{O}$  was studied by A. and H. Benrath, H. Weiland, and H. Hamacher. A. and H. Benrath's results are summarized in Fig. 136, where the region of the 1 : 1 : 6 double salt is stippled.  $\text{Co}_1$ ,  $\text{Co}_6$ , and  $\text{Co}_7$ , respectively, refer to the mono-, hexa-, and the hepta-hydrates of cobalt sulphate. F. R. Mallet prepared crystals of the anhydrous salt by fusing mixtures of the com-

to A. E. H. Tutton, the crystals of the *hexahydrate* belong to the monoclinic system, and have the axial ratios  $a : b : c = 0.7413 : 1 : 0.4995$ , and  $\beta = 106^\circ 25'$ . The cleavage parallel to the (201)-face is well developed; and that parallel to the (010)-face is feeble. The optic axial angles are :

	Li-	C-	Na-	Tl-	F-light
$2E$	$122^\circ 49'$	$123^\circ 13'$	$125^\circ 31'$	$127^\circ 27'$	—
$2H_a$	$63^\circ 45'$	$63^\circ 46'$	$64^\circ 2'$	$64^\circ 12'$	—
$2H_o$	$108^\circ 39'$	$108^\circ 33'$	$107^\circ 30'$	$106^\circ 24'$	—
$2\Gamma_a$	$66^\circ 3'$	$66^\circ 7'$	$66^\circ 39'$	$67^\circ 8'$	$68^\circ 0'$

O. Pettersson gave for the sp. gr. 3.729 at  $16.2^\circ$  to 3.803 at  $16.4^\circ$ ; and A. E. H. Tutton, 3.782 at  $20^\circ/4^\circ$ ; the mol. vol., 201.40; and the mol. distance ratios, i.e. the topic axial ratios, are  $\chi : \psi : \omega = 6.1356 : 8.2769 : 4.1344$ . The refractive indices are :

	Li-	C-	Na-	Tl-	F-	G-light
$\alpha$	1.5959	1.5965	1.6009	1.6061	1.6121	1.6197
$\beta$	1.6122	1.6128	1.6176	1.6231	1.6293	1.6369
$\gamma$	1.6182	1.6188	1.6238	1.6294	1.6359	1.6435

The mean refractive index for Na-light is 1.6141; and the double refraction  $\gamma - \alpha = 0.6229$ . The general formula for  $\beta$  is  $\beta = 1.5951 + 714.173\lambda^{-2} + 2,804,900,000\lambda^{-4} + \dots$ . The index  $\alpha$  is reproduced if the constant 1.5951 is diminished by 0.0167, and the index  $\gamma$ , if it is increased by 0.0062. The sp. refractions with the  $\mu^2$ -formula for the  $C(H_a)$ - and the  $H_\gamma$  (near G)-rays are, respectively,  $\alpha = 0.0900$ , and  $0.0928$ ;  $\beta = 0.0920$ , and  $0.0949$ ; and  $\gamma = 0.0927$ , and  $0.0957$ ; and the mol. refractions,  $\alpha = 68.57$ , and  $70.72$ ;  $\beta = 70.08$ , and  $72.28$ ; and  $\gamma = 70.63$ , and  $72.88$ ; the sp. dispersions for G- and C-rays,  $\alpha = 0.0028$ ,  $\beta = 0.0029$ , and  $\gamma = 0.0030$ ; and the mol. dispersions,  $\alpha = 2.15$ ,  $\beta = 2.20$ , and  $\gamma = 2.25$ . The mol. dispersions by the  $\mu$ -formula are  $\alpha = 120.13$ ,  $\beta = 123.42$ , and  $\gamma = 124.62$ , mean 122.72.

H. Vohl reported crystals of **ammonium manganous cobaltous sulphate**,

$2(\text{NH}_4)_2\text{SO}_4 \cdot \text{MnSO}_4 \cdot \text{CoSO}_4 \cdot 12\text{H}_2\text{O}$ , and of **potassium manganous cobaltous sulphate**,  $2\text{K}_2\text{SO}_4 \cdot \text{CoSO}_4 \cdot 12\text{H}_2\text{O}$ , to be formed from mixed soln. of the component salts. What evidence is available with other salts favours the assumption that these products are solid soln. J. W. Retgers investigated the complete series of solid soln. formed with the heptahydrated cobaltous and ferrous sulphates; and there is no sign of the formation of a **ferrous cobaltous sulphate**. A. Étard reported **ferrous cobaltous hydrosulphate**,  $2\text{FeSO}_4 \cdot 2\text{CoSO}_4 \cdot \text{H}_2\text{SO}_4$ , to be formed by treating a sat. soln. of the component salts with a large excess of cold sulphuric acid. B. Gossner and M. Arm reported,  $\text{K}_2\text{H}_{10}(\text{SO}_4)_6 \cdot 3\text{Fe}(\text{OH})_3 \cdot 4\text{CoSO}_4 \cdot 4\text{H}_2\text{O}$ . H. G. K. Westenbrink observed that the introduction of cobalt sulphate in ferrous sulphate has very little influence on the space-lattice of ferrous sulphate. H. Vohl reported **ammonium ferrous cobaltous sulphate**,  $2(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot \text{CoSO}_4 \cdot 12\text{H}_2\text{O}$ , and **potassium ferrous cobaltous sulphate**,  $2\text{K}_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot \text{CoSO}_4 \cdot 12\text{H}_2\text{O}$ , but these products may be solid soln.

J. G. Gentele<sup>3</sup> found that a conc. soln. of cobaltous sulphate gives a green precipitate of **cobaltous oxysulphate**,  $\text{Co}_2\text{O}_3 \cdot 6\text{CoSO}_4 \cdot 15\text{H}_2\text{O}$ , when treated with conc. aq. ammonia, and the precipitate gradually passes into soln. Water re-precipitates a similar product.

P. C. Ray and P. B. Sarkar<sup>4</sup> prepared monoclinic crystals of **ammonium cobalt sulphatofluoberyllate**,  $(\text{NH}_4)_2\text{BeF}_4 \cdot \text{CoSO}_4 \cdot 6\text{H}_2\text{O}$ , and of **potassium cobalt sulphatofluoberyllate**,  $\text{K}_2\text{BeF}_4 \cdot \text{CoSO}_4 \cdot 6\text{H}_2\text{O}$ , in isomorphous series with Ni, Fe, Mn, Cd, Zn, and Mg in place of Co. H. Siefert studied the crystals.

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## § 24. Cobaltic Sulphate and its Complex Salts

H. Marshall<sup>1</sup> prepared hydrated cobaltic sulphate,  $\text{Co}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ , by the electrolysis of a sat. soln. of cobaltous sulphate in dil. sulphuric acid (1 : 8) in a platinum dish as anode, and as cathode, a piece of platinum wire in a porous cell containing dil. sulphuric acid. E. Oberer, H. Copaux, and S. Swann and T. S. Xanthakos also prepared this salt electrolytically. E. Oberer studied the

theory of the process. Other things being equal, increasing the concentration of the acid in the electrolyte from  $\frac{1}{3}N$ - to  $5N$ - $H_2SO_4$ , raised the proportion of  $Co^{+++} : Co^{++}$  from 0.26 : 1 to 2.72 : 1; increasing the concentration of the cobaltous salt from 0.005 to 0.133 gram-atom lowered the proportion of  $Co^{+++} : Co^{++}$  from 5.43 : 1 to 3.45 : 1; lowering the temp. from  $30^\circ$  to  $-7^\circ$ , raised the proportion  $Co^{+++} : Co^{++}$  from 0.24 : 1 to 7.22 : 1; and raising the current density from 0.5 amp. to 1 amp. to 2 amp., altered the ratio  $Co^{+++} : Co^{++}$  from 1.48 : 1 to 1.77 : 1 to 1.18 : 1. The potential of the cobaltous-cobaltic sulphate soln. referred to the normal hydrogen electrode, was studied by A. B. Lamb and A. T. Larson. E. Oberer found that in the presence of  $2N$ - $H_2SO_4$ , for soln. with  $C$  grms. of the salts in 50 c.c. of water :

$Co^{+++}$	.	.	.	.	0.102	0.103	0.287
$Co^{++}$	.	.	.	.	1.372	0.171	0.260
Maximum potential	.	.	.	.	-1.705	-1.741	-1.759 volts

H. Marshall observed that cobaltic sulphate collects about the anode in a dry atmosphere, or if gently warmed, it loses water, and rapidly decomposes, becoming first of a brownish colour, which quickly gives place to pink. If kept in a moderately moist atmosphere, this does not take place nearly so readily; some which has been kept in a tightly-stoppered tube for months does not show any signs of decomposition. Treated with water, it dissolves, but immediately begins to decompose, becoming of a dark purplish colour, quickly changing to a greyish, neutral tint, and ultimately becoming pink. The oxygen liberated is evolved briskly during the process. The greyish tint seems to indicate that the colours of the cobaltous and cobaltic salts are nearly complementary. S. R. Benedict obtained what he regarded as a soln. of nickelic sulphate, by digesting nickelic oxide with a nearly sat. soln. of potassium hydrosulphate, but not so with cobaltic sulphate. A. Mailfert noted the formation of a brown precipitate when ozone acts on a feebly acidic soln. of cobalt sulphate, and P. Jannasch and W. Gottschalk regarded the precipitate as hydrated cobaltic oxide. E. Brunner, and S. Jahn discussed the formation of a soln. of cobaltic sulphate by the action of ozonized oxygen on a soln. of cobalt sulphate. The formation of the crystals by oxidizing a soln. of cobalt sulphate with fluorine, was described by F. Fichter and co-workers, E. Oberer, N. C. Jones, and W. D. Bancroft and N. C. Jones. H. Wolfmann obtained cobaltic sulphate by the action of fluorine on a sulphuric acid soln. of cobaltous fluoride :

A soln. of 2.4 grms. of heptahydrated cobaltous fluoride in 1.5 c.c. of  $8N$ - $H_2SO_4$ , at  $30^\circ$ , was treated with fluorine whilst the soln. was slowly cooling to  $0^\circ$ . The soln. becomes brown, then green, and then acicular crystals, with a silky lustre, are formed. In about  $1\frac{1}{2}$  hrs., the platinum crucible contains bluish-green crystals of cobaltic sulphate; and there is a risk of choking the inner tube by the formation of these crystals.

J. Topp observed two bands at  $612m\mu$  and  $400m\mu$  in the absorption spectrum in the visible region; and a band at  $300m\mu$  in the ultra-violet. E. Miescher also studied the absorption spectrum. E. Oberer studied the decomposition of the green, aq. soln. of cobaltic sulphate whereby oxygen is developed and cobaltous sulphate is formed, by a reaction which is symbolized :  $Co_2(SO_4)_3 + H_2O = 2CoSO_4 + H_2SO_4 + O$ . The velocity constants,  $k_1$  and  $k_2$ , on the assumption that the reaction is, respectively, of the first and second orders, are :

Time	.	15	60	120	180	240	345 mins.
$k_1$	.	0.00201	0.00188	0.00192	0.00179	0.00163	0.00132
$k_2$	.	0.00119	0.00132	0.00152	0.00164	0.00164	0.00144

Neither of the results for  $k_1$  and  $k_2$  is conclusive, but it is thought that they agree best with the assumption that the reaction is of the first order, and that it is retarded by the increasing concentration of the acid produced in the reaction. The electrode potential of soln. in  $2N$ - $H_2SO_4$ , with platinum electrodes at  $0^\circ$ , is 1.759 volt for a soln. with 0.287 gm.  $Co^{+++}$  and 0.260 gm.  $Co^{++}$  in 50 c.c. R. H. Weber found the mol. magnetic susceptibility to be  $4860 \times 10^{-6}$  mass unit.

H. Marshall observed that cobaltic sulphate dissolves very easily, and without

immediate decomposition, in dil. sulphuric acid. Such a soln. is greenish-blue, but gradually decomposes completely in the course of a day or two. It is, of course, very easily decomposed by all reducing agents. It gives a black precipitate when alkali is quickly added. The solid is also soluble in conc. acetic and nitric acids. Conc. sulphuric acid dissolves it, with formation of a deep reddish-brown solution. With hydrochloric acid, cobaltous salt and chlorine are formed. In agreement with H. Marshall, H. Wolfmann observed that ice-cold water rapidly decomposes the salt, and with warm water, the decomposition is instantaneous:  $\text{Co}_2(\text{SO}_4)_3 + \text{H}_2\text{O} = 2\text{CoSO}_4 + \text{H}_2\text{SO}_4 + \text{O}$ . M. Wikul prepared a salt corresponding with **cobaltyl sulphate**,  $(\text{CoO})_2\text{SO}_4$ . S. Jahn found that ozone decomposes the soln. until a state of equilibrium is attained:  $\text{Co}^{++} \rightleftharpoons \text{Co}^{+++}$ . E. Oberer found that the decomposition of the aq. soln. is accelerated by the catalytic action of finely-divided platinum, and by the addition of cobaltous sulphate. H. Marshall, F. Fichter and H. Wolfmann, and E. Brunner observed that soda-lye gives a black precipitate; hydrochloric acid dissolves the salt, forming a blue soln. which gives off chlorine; with potassium iodide, iodine is liberated; dil. sulphuric acid forms a green soln. in the cold, which decomposes when warmed; conc. sulphuric acid forms a reddish-brown soln.; conc. nitric acid forms a green soln., which becomes red when warmed; dil. nitric acid immediately decomposes the salt; acetic acid forms a green soln.; glycerol forms a rose-red soln.; ethyl alcohol immediately decomposes the salt—H. Copaux added that the alcohol is oxidized to aldehyde; and the salt is insoluble in ether and in carbon disulphide, and both liquids rapidly decompose the salt. A. Naumann and J. Schröder said that the sulphate is insoluble in pyridine.

H. Marshall, and E. Oberer prepared **ammonium cobaltic disulphate**,  $\text{NH}_4\text{Co}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , or *cobaltic alum*,  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Co}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ . H. Marshall said: The sulphate was electrolyzed till a large quantity of cobaltic salt had separated. The temp. was then allowed to rise to about  $20^\circ$ , and dil. acid added to dissolve the solid which still remained. The roughly-calculated quantity of ammonium sulphate in fine powder was now added (only a small proportion of the cobalt passes to the inner cell) and a weak current passed until this was practically all dissolved. The clear liquid was then decanted and cooled by a freezing mixture. In this way a large crop of minute, octahedral crystals of the alum was obtained. By more slowly cooling, larger crystals, recognizable with the naked eye, or easily with a hand-lens, separated; they had a fine, deep blue colour. That they were regular octahedra was shown by their behaviour in polarized light. F. Müller observed that the vap. press. of the salt,  $p$  mm., is 6.5 at  $15^\circ$ , 40 at  $28^\circ$ , and 91 at  $35.5^\circ$ . H. Marshall, and E. Oberer prepared **potassium cobaltic disulphate**,  $\text{KCo}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , by the method employed for the ammonium salt; and H. Copaux, by mixing eq. proportions of well-cooled soln. of the component salts, and washing the crystalline precipitate, first with acetic acid, and then with acetone. H. Marshall added that the alums behave towards water and acids like the cobaltic sulphate. They also decompose when they lose water. The crystals cannot be completely freed from mother-liquor by a porous plate, but may subsequently be pressed between filter-paper, with which, however, they must not be left long in contact.

J. L. Howe and E. A. O'Neal, and E. Oberer prepared **rubidium cobaltic disulphate**,  $\text{RbCo}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , by electrolyzing a soln. of the component sulphates acidified with sulphuric acid; and H. Copaux, by mixing soln. of the component sulphates as in the case of the potassium salt. The deep blue, octahedral crystals are stable in dry air, but decompose in moist air. J. Locke found the m.p. to be  $47^\circ$ . In water, oxygen and cobaltous sulphate are formed; blue soln. are formed with dil. hydrochloric or sulphuric acid, and decomposition, with the formation of a brown soln., occurs in the presence of conc. hydrochloric or sulphuric acid. J. L. Howe and E. A. O'Neal, and E. Oberer also prepared pale greenish-blue crystals of **cæsium cobaltic disulphate**,  $\text{CsCo}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , in a similar manner. J. Locke found the m.p. to be  $63^\circ$ . F. Ephraim and P. Wagner found the vap.



press. to be 4 mm. at 27°, and 25 mm. at 39°; whilst above 40°, the salt decomposes, with the evolution of oxygen, and the green crystals become rose-red. J. Locke found that a litre of water at 25°, dissolves 418.8 grms. of the anhydrous salt. J. L. Howe and E. A. O'Neal said that the salt is readily decomposed by water, with the evolution of oxygen, and that the behaviour of the salt towards dil. and conc. hydrochloric and sulphuric acids resembles that of the rubidium salt. M. Wikul prepared **sodium cobaltyl sulphate**,  $(\text{CoO})_2\text{SO}_4 \cdot \text{NaHSO}_4$ .

### The $\text{CoA}_6$ or Hexammine Family

E. Frémy,<sup>2</sup> J. G. Gentile, and O. W. Gibbs and F. A. Genth prepared **cobaltic hexamminesulphate**,  $[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ , by oxidizing an ammoniacal soln. of a mixture of cobaltous sulphate and chloride with air, and digesting the product with a soln. of silver sulphate in dil. sulphuric acid; or by treating the aquopentamminesulphate with aq. ammonia. L. Jacobsen used lead dioxide as oxidizing agent with an ammoniacal soln. of ammonium cobaltous sulphate; and S. M. Jørgensen saturated the corresponding chloride with freshly-prepared silver oxide, and then treated the filtrate with dil. sulphuric acid; or direct from a soln. of the chloride and sulphuric acid, followed by the addition of alcohol. T. Klobb, and F. M. Jäger found that the crystals are monoclinic prisms, with the axial ratios  $a : b : c = 1.1230 : 1 : 1.4143$ , and  $\beta = 90^\circ 18'$ ; J. D. Dana thought that they were rhombic. E. Birk and W. Biltz found the sp. gr. of the anhydrous salt is 1.797 at 25°/4°; and the mol. vol. is 339.8. The mol. vol. of the  $\text{NH}_3$ -groups is 18.65 when that of the corresponding cobaltous salt is 19.10. The subject was also discussed by W. Biltz. Analyses indicate that the air-dried crystalline product is the *pentahydrate*; E. Frémy, and J. G. Gentile, regarded the salt as a *tetrahydrate*. S. M. Jørgensen observed that the air-dried salt loses 4 mols. of water over conc. sulphuric acid, or at 100°, and the remaining molecule of the monohydrate is lost at 150°. A. Benrath and W. Kohlberg's observations are summarized in Fig. 137.

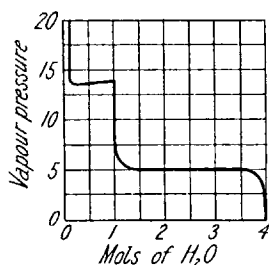


FIG. 137.—The Vapour Press of the Pentahydrate.

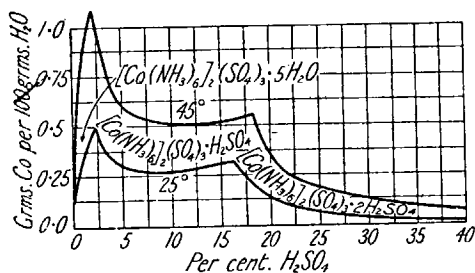


FIG. 138.—The Solubility of the Hexamminesulphate in Sulphuric Acid.

W. Biltz said that the salt loses its water of hydration at 150°; it remains constant in weight up to 193°; and it gives off all the ammonia at 213°. The polarization tension was studied by N. R. Dhar and G. Urbain. E. Feytis gave  $-0.315 \times 10^{-6}$  mass unit for the magnetic susceptibility.

S. M. Jørgensen found that at 17.4°, 100 parts of water dissolve 1.41 parts of salt, and at 20°, 1.61 parts; F. Ephraim, P. Mosimann, and F. Ephraim and P. Mosimann said that at 18°, a sat. soln. has 0.015 mol or 1.792 grms. per litre; and J. N. Brønsted and A. Petersen gave 0.009 mol per litre at 0°, and 0.020 mol per litre at 20°. The subject was discussed by L. A. Hansen and J. W. Williams. The aq. soln. was found by O. W. Gibbs and F. A. Genth, and S. M. Jørgensen to be very stable, since on boiling the aq. or feebly ammoniacal soln., no perceptible decomposition occurs. A sat., aq. soln. gives a precipitate of the sulphate and chloride when treated with hydrochloric acid; potassium iodide precipitates an iodosulphate; but sulphuric acid gives no precipitate. According to A. Benrath,

and A. Benrath and H. Würzburger, the solubility determinations in sulphuric acid, Fig. 137, show that three solid phases may exist. With soln. containing up to 2.5 per cent.  $\text{H}_2\text{SO}_4$ , the solid phase is the *pentahydrate*; with between 2.5 and 19.0 per cent.  $\text{H}_2\text{SO}_4$ , the solid phase is **cobaltic hexamminosulphatodihydrosulphate**,  $[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4$ , which forms prismatic crystals. Alcohol precipitates the normal sulphate from hot, aq. soln. The third phase is **cobaltic hexamminosulphatetetrahydrosulphate**,  $[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3 \cdot 2\text{H}_2\text{SO}_4$ , stable in soln. with more than 19 per cent.  $\text{H}_2\text{SO}_4$ . By adding an excess of sulphuric acid to a soln. of the normal sulphate, T. Klobb obtained **cobaltic hexamminosulphatodecahydrosulphate**,  $2[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , in cubic crystals belonging to the rhombic bipyramidal system, with axial ratios  $a : b : c = 0.9991 : 1 : 1.0006$ . F. M. Jäger also made observations on the crystals. According to A. Benrath and H. Würzburger, the existence of this salt is doubtful. P. B. Sarkar and T. P. Barat prepared these three acid salts. F. Ephraim observed no evidence indicating that ammonia is taken up by the salt at  $-21^\circ$ . O. W. Gibbs and F. A. Genth, and S. M. Jörgensen found that a sat. aq. soln. of the salt with nitric acid gives a mixed precipitate of sulphate and nitrate; hydrochloroplatinic acid precipitates a chlorosulphatinate; and yellow or brownish-yellow precipitates are formed with hydrosilicic acid, hydrochloroauric or hydrobromoauric acid, and with potassium dichromate.

Some double salts have been reported. T. Klobb reported octahedral or tabular crystals of **ammonium cobaltic hexamminosulphate**,  $\text{NH}_4[\text{Co}(\text{NH}_3)_6](\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ , to be formed from a soln. of the component sulphates. The rhombic crystals have tetragonal symmetry, and the axial ratios  $a : b : c = 0.9747 : 1 : 1.993$ . The crystals were discussed by P. Groth, and F. M. Jäger. P. B. Sarkar and T. P. Barat prepared **potassium cobaltic hexamminosulphate**,  $\text{K}_2\text{SO}_4 \cdot [\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$ . F. Ephraim and P. Mosimann doubted the existence of this salt. O. W. Gibbs reported **thallium cobaltic hexamminosulphate**,  $[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3 \cdot \text{Tl}_2\text{O}(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$ , in yellow scales resembling talc; C. H. Wing reported yellow powders of **cerous cobaltic hexamminosulphate**,  $[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3 \cdot 3\text{CeSO}_4 \cdot \text{H}_2\text{O}$ ; **eerie cobaltic hexamminosulphate**,  $[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3 \cdot \text{Ce}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ ; and **lanthanous cobaltic hexamminosulphate**,  $[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3 \cdot 3\text{LaSO}_4 \cdot \text{H}_2\text{O}$ .

J. B. Rogojsky reported **cobaltic hexamminochlorosulphate**,  $[\text{Co}(\text{NH}_3)_6](\text{SO}_4)\text{Cl} \cdot 3\text{H}_2\text{O}$ , to be formed by treating the corresponding chloride with silver sulphate in the cold, and evaporating the filtrate over sulphuric acid. H. Schiff obtained the salt from eq. proportions of soln. of chloride and sulphate; J. M. Krok, by the action of chlorine on the iodosulphate; L. Jacobsen, by the action of chlorine or of silver chloride on an ammoniacal soln. of ammonium cobaltous sulphate; and T. Klobb, from a soln. of the corresponding chloride with dil. sulphuric acid or a sulphate, or from a soln. of the corresponding sulphate with dil. hydrochloric acid or a chloride. O. W. Gibbs and F. A. Genth considered that the salt is not a chemical individual, but rather a solid soln. of variable composition. The reddish-yellow rectangular prisms belong to the rhombic system. T. Klobb gave for the axial ratios,  $a : b : c = 0.9986 : 1 : 1.0538$ , and T. V. Barker,  $0.9983 : 1 : 1.0567$ . The crystals were also discussed by P. Groth and G. N. Wyruboff. O. Hassel and G. B. Naess examined the X-radiograms and showed that the crystals possess rhombic symmetry about the  $c$ -axis. T. V. Barker gave  $1.765$  for the sp. gr., and  $196.29$  for the mol. vol. A. Benrath and W. Kohlberg found that the vap. press. curve showed the existence of the *trihydrate*, but not of the *hemihydrate* reported by H. Schiff. O. Stelling studied the X-ray spectrum. T. Klobb, and O. W. Gibbs and F. A. Genth found that the salt is sparingly soluble in cold water, and less soluble than either the normal sulphate or chloride. J. N. Brönsted and A. Petersen said that at  $0^\circ$  a sat. soln. contains  $0.01055$  mol per litre. T. Klobb reported octahedral crystals of **ammonium cobaltic hexamminochlorosulphate**,  $[\text{Co}(\text{NH}_3)_6]_4(\text{SO}_4)_5\text{Cl}_2 \cdot 3(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ , by spontaneously evaporating a mixed soln. of the chlorosulphate and ammonium sulphate. The cubic (hexakisoctahedral) crystals of the salt were discussed by F. M. Jäger. There is some doubt about its individuality. S. M. Jörgensen reported **gold cobaltic hexamminochlorosulphate**,  $[\text{Co}(\text{NH}_3)_6](\text{SO}_4)(\text{AuCl}_4)$ ,

in orange-yellow, dichroic, rectangular prisms. J. M. Krok reported **mercuric cobaltic hexamminochlorosulphate**,  $[\text{Co}(\text{NH}_3)_6](\text{SO}_4)\text{Cl}.\text{HgCl}_2$ , to be formed in small, yellow prisms from soln. of the component salts.

S. M. Jörgensen reported **cobaltic hexamminobromosulphate**,  $[\text{Co}(\text{NH}_3)_6](\text{SO}_4)\text{Br}$ , to be formed from a soln. of the corresponding bromide and dil. sulphuric acid or ammonium sulphate; or from a soln. of the corresponding sulphate and dil. hydrobromic acid or ammonium bromide. The brownish-yellow, octahedral crystals reported by S. M. Jörgensen were found by O. Hassel, and O. Hassel and G. B. Naess to be cubic, with a face centred lattice having the parameter  $a=10.51$  Å. The structure was also discussed by F. Ephraim and W. Flügel; the anomalous birefringence, by O. Hassel and G. B. Naess. S. M. Jörgensen reported **gold cobaltic hexamminobromosulphate**,  $[\text{Co}(\text{NH}_3)_6](\text{SO}_4)(\text{AuBr}_4)$ , to be formed in brownish-black, dichroic needles or plates, from soln. of the component salts.

C. W. Blomstrand, and J. M. Krok obtained **cobaltic hexamminiodosulphate**,  $[\text{Co}(\text{NH}_3)_6](\text{SO}_4)\text{I}$ , by boiling an ammoniacal soln. of cobaltous and ammonium sulphates, and iodine, and crystallizing the precipitate from hot water; and F. Ephraim and W. Flügel, by adding, drop by drop, a soln. of potassium iodide to one of the corresponding sulphate. O. Hassel and G. B. Naess, and O. Hassel found the yellow, octahedral crystals are isotropic and belong to the cubic system. The X-radiograms show that the face-centred lattice has 4 mols. in the unit cell, which has the parameter  $a=10.71$  Å., that the  $\text{NH}_3$ -groups are arranged at the apices of regular octahedron about the cobalt atoms, and that four oxygen atoms are grouped about one sulphur atom. The structure resembles that of fluorspar with the complex cobalt cation in place of the Ca-atom, and the  $\text{SO}_4$ -groups and I-atoms in place of the F-atoms. The structure was also studied by F. Ephraim and W. Flügel. J. M. Krok added that the hot, aq. soln. gives yellow, crystalline precipitates with hydrofluosilicic acid, with potassium chromate, dichromate, or oxalate, and with sodium hydrophosphate; greyish-green precipitates with potassium ferrocyanide or ferricyanide; and mercuric chloride precipitates mercuric iodide. Chlorine displaces the iodine, but not so bromine.

A. Werner and E. Berl<sup>3</sup> obtained **cobaltic hexahydroxylaminesulphate**,  $[\text{Co}(\text{NH}_2\text{OH})_6]_2(\text{SO}_4)_3.2\text{H}_2\text{O}$ , by adding conc. sulphuric acid to a well-cooled (say,  $-15^\circ$  to  $-20^\circ$ ) soln. of the corresponding chloride. The small, yellow crystals are readily soluble in water, and decompose at  $90^\circ$  to  $100^\circ$ .

J. Meyer and K. Gröhler,<sup>4</sup> and L. Lehrfeld prepared **cobaltic triethylenediaminesulphate**,  $[\text{Co en}_3]_2(\text{SO}_4)_3.2\text{H}_2\text{O}$ , by adding alcohol to a soln. of the hydrosulphate. The yellow, crystalline powder is readily soluble in water; it is stable in contact with dil. mineral acids; sulphuric acid does not precipitate the salt from its aq. soln.; with nitric or hydrochloric acid, a mixed sulphate and nitrate or chloride separates from the soln. Boiling the aq. soln. is attended by decomposition; and the solid salt blackens at  $150^\circ$ . J. Meyer and K. Gröhler obtained **cobaltic triethylenediaminehydrosulphate**,  $[\text{Co en}_3](\text{HSO}_4)_3$ , by dissolving 7 grms. of the corresponding chloride in 60 c.c. of cold, conc. sulphuric acid, and after standing over sulphuric acid and potassium hydroxide, in vacuo, for 24 hrs., pouring the soln. into ice-cold, absolute alcohol. If a soln. of 4.5 grms. of sulphatohydrosulphate, in 40 c.c. of ice-cold sulphuric acid, be poured into ice-cold, absolute alcohol, this salt is produced in pale yellow crystals. If a soln. of 5 grms. of this hydrosulphate, in 40 c.c. of 20 per cent., ice-cold sulphuric acid, or a soln. of 3 grms. of the normal sulphate, in 35 c.c. of 25 per cent., ice-cold sulphuric acid, be poured into ice-cold, absolute alcohol **cobaltic triethylenediaminesulphatohydrosulphate**,  $[\text{Co en}_3](\text{SO}_4)(\text{HSO}_4). \frac{1}{2}\text{H}_2\text{O}$ , is formed as a pale yellow oil, which can be crystallized by rubbing with a glass rod. F. M. Jäger and P. Koets reported **cobaltic triethylenediaminechlorosulphate**,  $[\text{Co en}_3]_2(\text{SO}_4)\text{Cl}.5\text{H}_2\text{O}$ , to be formed by adding the theoretical proportion of silver sulphate to a soln. of the corresponding chloride. The ditrigonal crystals have the axial ratio  $a : c = 1 : 3.0285$ , and  $\alpha = 51^\circ 0'$ .

F. M. Jäger obtained **cobaltic phenanthrolinebisethylenediaminesulphate**,  $[\text{Co en}_2(\text{C}_{12}\text{H}_8\text{N}_2)]_2(\text{SO}_4)_3.12\text{H}_2\text{O}$ , in pale brown crystals, by adding silver sulphate to the corresponding iodide. The triclinic crystals have the axial ratios  $a : b : c = 1.4062 : 1 : 0.7362$ . If a conc. soln. of chloroaquobisethylenediaminesulphate be heated with  $\alpha$ -phenanthroline for 6 to 8 hrs., golden-yellow, dichroic, triclinic needles of **cobaltic**

phenanthrolinebisethylenediaminechlorosulphate,  $[\text{Co}_2\text{en}_4(\text{C}_{12}\text{H}_8\text{N}_2)]_2(\text{SO}_4)\text{Cl}\cdot 2\text{H}_2\text{O}$ , are formed. F. M. Jäger and P. Koets digested the chloroaquobisethylenediaminesulphate with an aq. soln. of triaminotriethylamine for 4 hrs., and then treated the soln. with silver sulphate, when brownish-red, dichroic, octahedral crystals of **cobaltic bistriaminotriethylaminesesiesethylenediaminesulphate**,  $[\text{Co}_2\text{en}_4(\text{C}_6\text{H}_{18}\text{N}_4)]_2(\text{SO}_4)_3\cdot 8\text{H}_2\text{O}$ , were formed. The axial ratios of the rhombic bipyramids were  $a : b : c = 1.0131 : 1 : 1.1277$ . The lowering of the f.p. of aq. soln. corresponds with a mol. wt. of 261.6, and an 85 per cent. ionization. The mol. wt. for 11 ions is 242. The mol. conductivity,  $\mu$ , and the degree of ionization,  $\alpha$ , of soln. of a mol in  $v$  litres, are :

$v$	53.22	77.22	102.98	137.36	183.15	366.20	109.89
$\mu$	1210	1397	1450	1548	1635	1802	2769
$\alpha$	0.43	0.50	0.52	0.55	0.59	0.65	1.0

F. M. Jäger and P. Koets also prepared brown rhombohedra of **cobaltic bistriaminotriethylaminesesiesethylenediaminechlorosulphate**,  $[\text{Co}_3\text{en}_6(\text{C}_6\text{H}_{18}\text{N}_4)]_2(\text{SO}_4)_3\text{Cl}_{12}\cdot 10\text{H}_2\text{O}$ , belonging to the trigonal system, and having the axial ratio  $a : c = 1 : 3.0114$ , and  $\alpha = 51^\circ 10'$ . G. Spacu and R. Ripan prepared some complex pyridine salts.

E. Frémy<sup>5</sup> appears to have obtained **cobaltic aquopentamminosulphate**,  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]_2(\text{SO}_4)_3\cdot 3\text{H}_2\text{O}$ , in 1852, by crystallization from an aq. soln. of the hydrosulphate; P. Job used a similar process; O. W. Gibbs and F. A. Genth prepared the salt by adding conc. sulphuric acid to an oxidized ammoniacal soln. of cobaltous sulphate; S. M. Jörgensen, by evaporating a soln. of the corresponding carbonate or oxalate in  $N\text{-H}_2\text{SO}_4$ , and evaporating for crystallization over sulphuric acid, or precipitating the salt from its aq. soln. by alcohol; and P. Job, by the action of sulphuric acid on an ice-cold soln. of the corresponding pyrophosphate, and afterwards adding alcohol to precipitate the sulphate. O. W. Gibbs reported an isomeric, yellow variety, but S. M. Jörgensen could not confirm this result. The red, quadratic crystals, according to F. M. Jäger, are tetragonal, with the axial ratio  $a : c = 1 : 1.0862$ , sp. gr. 1.854 at  $20^\circ$ , mol. vol. 359.22; and topic axial ratios  $\chi : \psi : \omega = 6.9155 : 6.9155 : 7.5115$ . H. Skraup and co-workers measured the capillary rise of aq. soln. A. Werner found that the solid salt is quite stable when kept; and S. M. Jörgensen, that when dried over sulphuric acid, the salt gains 2.5 mols. of water, and it loses 3 mols. of water at  $90^\circ$ , without losing its acidic character. E. Frémy said that the total amount of water in the salt is  $3\text{H}_2\text{O}$ , but O. W. Gibbs and F. A. Genth, and C. D. Braun showed that 5 mols. in all are present; and on A. Werner's system, the salt appears as a *trihydrate*, 2 mols. belong to the two complex cations of the salt. This was confirmed by A. Benrath and W. Kohlberg's vap. press. measurements, where there is an abrupt break in the curve, corresponding with the hydrate, which he formulated:  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})](\text{SO}_3\cdot\text{H}_2\text{O})_3$ . The *tetrahydrate* reported by G. Vortmann, and C. D. Braun, was not observed by A. Benrath and W. Kohlberg. According to S. M. Jörgensen, when the salt is dehydrated beyond the trihydrate stage, it forms sulphatopentamminosulphate, and at  $110^\circ$ , some tetrammine is formed as well. P. Job also studied the dehydration of the salt at  $75^\circ$ . According to K. Matsuno, the mol. conductivity,  $\mu$ , of soln. with a mol of the salt in  $v$  litres, at  $25^\circ$ , is :

$v$	100	200	400	800	1600
$\mu$	117.0	151.8	182.2	217.0	265.1

when the soln.  $v=100$  is kept for an hour, the conductivity rises from 117.0 to 143.5; this indicates that the salt is not stable in aq. soln. P. Job observed that the aquopentamminosulphate passes into the sulphato-sulphate, slowly at ordinary temp., but more rapidly at  $60^\circ$ ; and A. B. Lamb and J. W. Marden found that a 0.0087M-soln. of the aquopentamminosulphate, or of the sulphatopentammine sulphate, in 0.01M- $\text{H}_2\text{SO}_4$ , when kept 30 hrs. at  $70^\circ$ , contains 43.5 per cent. of aquopentamminosulphate, whichever salt was employed at the start. P. Job observed that in alkaline soln. the aquopentamminosulphate passes quantitatively into the hydroxypentamminosulphate. P. Job found the magnetic susceptibility to be  $-0.3 \times 10^{-6}$  mass unit.

S. M. Jörgensen observed that 100 grms. of water dissolve 1.057 grms. at 17.2°; 1.20 grms. at 20.2°; 1.38 grms. at 23°; and 1.72 grms. at 27°. F. Ephraim, and J. N. Brønsted and A. Petersen found that a sat., aq. soln. at 17.5° has 0.047 mol per litre; and F. Ephraim and W. Flügel, 0.16 mol per litre at 20°. According to P. Job, when a soln. of the aquopentamminosulphate is electrometrically titrated with barium hydroxide, the curve shows a singular point when one-third of the sulphuric acid has been precipitated, and another when all is precipitated. The reactions are symbolized:  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]_2(\text{SO}_4)_3 + \text{Ba}(\text{OH})_2 = [\text{Co}(\text{NH}_3)_5(\text{OH})]_2(\text{SO}_4)_2 + \text{BaSO}_4 + 2\text{H}_2\text{O}$ ; and the intermediate compound, isolated as indicated below, then reacts in accord with the equation:  $[\text{Co}(\text{NH}_3)_5(\text{OH})]_2(\text{SO}_4)_2 + 2\text{Ba}(\text{OH})_2 = [\text{Co}(\text{NH}_3)_5(\text{OH})]_2(\text{OH})_4 + 2\text{BaSO}_4$ .

The effect of sulphuric acid on the solubility was studied by A. Benrath and H. Würzburger, and their results are summarized by the curve, Fig. 139, with the

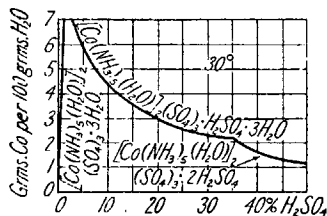


FIG. 139.—The Solubility of the Aquopentamminosulphate in Sulphuric Acid.

corresponding solid phases. A. Benrath added that at 30°, with soln. having up to 15 per cent.  $\text{H}_2\text{SO}_4$ , the solid phase is:  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]_2(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$ ; with 15 to 35 per cent.  $\text{H}_2\text{SO}_4$ , it is **cobaltic aquopentamminosulphatodihydrosulphate**,  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ ; and with over 35 per cent.  $\text{H}_2\text{SO}_4$ , **cobaltic aquopentamminosulphatetetrhydrosulphate**,  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]_2(\text{SO}_4)_3 \cdot 2\text{H}_2\text{SO}_4$ . Other acid salts have been described, but there are doubts about them.

Thus, E. Frémy, C. D. Braun, J. G. Gentile, O. W. Gibbs and F. A. Genth, and S. M. Jörgensen, refer to

$4[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ ; and the two salts described by P. Job,  $2[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{SO}_4 \cdot 12\text{H}_2\text{O}$ , and  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]_2(\text{SO}_4)_3 \cdot 3\text{H}_2\text{SO}_4$ , whose chemical individuality he doubted. P. Job and L. O. Tao observed that the solid phase is the salt itself; for soln. with 0 to 0.5 mol of  $\text{H}_2\text{SO}_4$  per litre, it is  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})](\text{SO}_4)(\text{HSO}_4) \cdot \text{H}_2\text{O}$ , in the cold, and at 56°, it is  $[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]\text{HSO}_4 \cdot 2\text{H}_2\text{O}$ . The tie lines for other concentrations are not concurrent, although nearly so for soln. with 4.5 to 8.5 mols  $\text{H}_2\text{SO}_4$  per litre.

According to A. Benrath, the effect of aq. ammonia at 50° to 75° is to convert the aquopentamminosulphate into the hexamminosulphate. K. Matsuno studied the flocculating action of the salt on the hydrosol of arsenic sulphide. S. M. Jörgensen observed that hydriodic acid forms an iodosulphate; hydrochloroplatinic acid, a chlorosulphatoplatinate; and hydrofluosilicic acid gives no precipitate. Otherwise, the general reactions are those characteristic of the family—*vide supra*, the aquopentamminochloride.

No description of **cobaltic aquopentamminochlorosulphate**,  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})](\text{SO}_4)\text{Cl}$ , is available, but J. M. Krok reported an **ammonium cobaltic aquopentamminochlorosulphate**,  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]_2\text{H}(\text{SO}_4)_3 \cdot \text{Cl} \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ , to be formed by passing chlorine into a soln. of the iodosulphate, and ammonium sulphate. The dark wine-red, octahedral crystals are easily soluble in water, and no decomposition occurs when the soln. is boiled. When heated with ammonium chloride and hydrochloric acid, the chloropentamminochloride is formed. S. M. Jörgensen obtained **gold cobaltic aquopentamminochlorosulphate**,  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})](\text{SO}_4)(\text{AuCl}_4)$ , in orange-red, dichroic, rectangular prisms, and J. M. Krok prepared **mercuric cobaltic aquopentamminochlorosulphate**,  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})](\text{SO}_4)\text{Cl} \cdot \text{HgCl}_2 \cdot 2\text{H}_2\text{O}$ , in prismatic crystals. G. Spacu and R. Ripan prepared complexes with **cobaltic magnesium aquoquinquesbenzylaminosulphate**,  $[\text{Co}(\text{C}_7\text{H}_5\text{N})_5(\text{H}_2\text{O})][\text{Co}(\text{H}_2\text{O})_6]\text{Mg}(\text{SO}_4)_3$ .

J. M. Krok prepared **cobaltic aquopentamminobromosulphate**,  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})](\text{SO}_4)\text{Br}$ , by the action of bromine on the iodosulphate; and S. M. Jörgensen, by precipitation on the addition of  $N\text{-H}_2\text{SO}_4$  to a cold, aq. soln. of the bromide. The yellowish-red, octahedral crystals were found, by S. M. Jörgensen, to be stable at 100°. According to O. Hassel and co-workers,

well-formed octahedral crystals can be obtained from ammoniacal soln.; and the X-radiograms show that the face-centred, cubic lattice has the parameter  $a=10.45$ . The structure is almost identical with that of the hexamminobromosulphate. S. M. Jörgensen prepared **gold cobaltic aquopentamminobromosulphate**,  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{SO}_4(\text{AuBr}_4)$ , in bronze-brown, dichroic needles.

O. W. Gibbs obtained **cobaltic aquopentamminiodosulphate**,  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})](\text{SO}_4)\text{I}$ , by adding potassium iodide to a soln. of the corresponding sulphate; J. Kranig, by adding potassium iodide to a soln. of the carbonato-sulphate; S. M. Jörgensen, and F. Ephraim and W. Flügel, by adding  $2N\text{-H}_2\text{SO}_4$  to an aq. soln. of the iodide; and O. Hassel and G. B. Naess, O. Hassel, J. M. Krok, and C. W. Blomstrand, by boiling an ammoniacal soln. of cobaltous sulphate with ammonium sulphate and iodine—the first crop of crystals is the hexamminiodosulphate, and the second crop, aquopentamminiodosulphate, which, on re-crystallization from ammoniacal soln., furnishes orange-red octahedra. O. Hassel, and O. Hassel and G. B. Naess observed that the X-radiograms indicate that the iododisulphate has a face-centred, cubic lattice, with edge  $a=10.62 \text{ \AA}$ , and with a structure quite analogous with that of the hexammines. F. W. Clarke and H. B. Wilson found the sp. gr. to be 2.139 to 2.149 at  $20.5^\circ$ . F. Ephraim and W. Flügel observed that a sat., aq. soln. has 0.0163 mol of the salt per litre at  $17^\circ$ . J. M. Krok showed that no water is lost at  $100^\circ$ , and that by evaporating a soln. in ammonia, the hexammino-salt is formed; the aq. soln. gives no precipitate with hydrofluosilicic acid, or with potassium chromate or dichromate, but a greyish-green turbidity is produced with potassium ferrocyanide or ferricyanide.

S. M. Jörgensen<sup>6</sup> prepared **cobaltic diaquotetramminosulphate**,  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]_2(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$ , by treating an aq. soln. of carbonatotetramminosulphate with dil. sulphuric acid, and then adding alcohol for precipitate; and J. V. Dubsy, by adding glacial acetic acid to a soln. of hydroxyaquotetramminosulphate in acetic acid. The small, red, quadratic prisms were thought by G. Vortmann to be a *dihydrate*; and by P. Job and L. O. Tao, a *hemipentahydrate*. A. Benrath and W. Kohlberg's measurements of the vap. press. indicate a *trihydrate*, and this agrees with A. Benrath and K. Andreas' observations on the solubility of the salt in sulphuric acid. S. M. Jörgensen found that over sulphuric acid, the salt loses 3 mols. of water without changing its general character, but when it loses the eq. of  $3\frac{1}{2}$  mols. of water at  $100^\circ$ , there is a fundamental change. A. Uspensky and K. Tschibisoff studied the absorption spectra of aq. soln. F. Ephraim said that a sat., aq. soln. has 0.175 mol per litre at  $22^\circ$ ; and A. Werner added that, unlike the chloride or bromide, the sulphate is quite stable and may be kept for a long time without change. S. M. Jörgensen regarded the hydroxy-aquotetramminosulphate as a basic salt. P. Job observed that in alkaline soln., the sulphate is hydrolyzed to form dihydroxytetramminosulphate. P. Job observed that when the soln. is electrometrically titrated with barium hydroxide, a singular point occurs in the curve when two-thirds of the sulphuric acid has been precipitated, and another singular point when all is precipitated. According to A. Benrath and K. Andreas, and K. Andreas, with soln. of sulphuric acid having between 0 and 35 per cent.  $\text{H}_2\text{SO}_4$ , the solid phase is the trihydrate,  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]_2(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$ ; when the soln. has between 35 and 80 per cent.  $\text{H}_2\text{SO}_4$ , the solid phase is **cobaltic diaquotetramminosulphatotetrahydrosulphate**,  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]_2(\text{SO}_4)_3 \cdot 2\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ ; and when over 80 per cent.  $\text{H}_2\text{SO}_4$  is present, cobaltic sulphatoaquotetramminosulphate is formed. P. Job and L. O. Tao indicated, without proof, the formation of  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]_7\text{H}(\text{SO}_4)_{11}$  and  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4$ . A. Benrath and K. Andreas also observed that aq. ammonia converts the diaquotetramminosulphate into hydroxypentamminosulphate; and A. Werner, that when heated with pyridine and very dil. acetic acid, the hexol-dodecammine is formed. A. Uspensky and K. Tschibisoff studied the action of carbon dioxide in converting the diaquotetramminosulphate into carbonatotetramminosulphate. F. Ephraim said that when the carbonatotetramminosulphate is treated with 25

per cent. hydrobromic acid until no more carbon dioxide is evolved, and the soln. in hydrobromic acid is cooled, **cobaltic diaquotetramminobromosulphate**,  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2](\text{SO}_4)\text{Br}$ , is formed as a red precipitate.

A. Werner and K. R. Lange prepared **cobaltic cis-diaquobisethylenediaminesulphate**,  $[\text{Co en}_2(\text{H}_2\text{O})_2]_2(\text{SO}_4)_3$ , in red needles, by the action of silver sulphate on the corresponding bromide; and **cobaltic trans-diaquobisethylenediaminesulphate**, in brown plates, by the action of conc. sulphuric acid on the cold soln. followed by the addition of water. The salt loses 2 mols. of water at  $80^\circ$  to  $90^\circ$ . A. Werner prepared **cobaltic diaquobispyridinediamminosulphatehydrosulphate**,  $[\text{Co}(\text{NH}_3)_2\text{Py}_2(\text{H}_2\text{O})_2]_2(\text{SO}_4)_3 \cdot 2\text{H}_2\text{SO}_4$ , in brownish-violet plates, from a soln. of chloride and conc. sulphuric acid. The red, aq. soln. has an acidic reaction.

### *The CoA<sub>5</sub> or Pentammine Family*

H. Schiff,<sup>7</sup> C. D. Braun, and S. M. Jörgensen prepared what they regarded as basic pentammino-salts; and P. Job obtained **cobaltic hydroxypentamminosulphate**,  $[\text{Co}(\text{NH}_3)_5(\text{OH})]\text{SO}_4 \cdot 2\text{H}_2\text{O}$ , by adding an eq. proportion of barium hydroxide, in aq. soln., to the aquopentamminosulphate, at  $0^\circ$ , and treating the filtrate with alcohol. The red, crystalline precipitate is stable when solid, but not so in aq. soln. In aq. soln., it behaves like a weak base—*vide supra*, aquopentamminosulphate. C. Duval obtained what he regarded as a persulphate, in which the  $\text{SO}_4$ -radicle is univalent,  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{SO}_4$ , but R. Klement showed that the product should be regarded as a hydroxyamminopersulphate,  $[\text{Co}(\text{NH}_3)_5(\text{OH})]\text{S}_2\text{O}_8$ .

S. M. Jörgensen obtained **cobaltic hydroxyaquotetramminosulphate**,  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{OH})]\text{SO}_4 \cdot \text{H}_2\text{O}$ , by adding alcohol to an ammoniacal soln. of the chloroaquotetramminosulphate, and he regarded it as a basic diaquotetrammine. A. Werner prepared it by adding sodium sulphate to a conc., aq. soln. of the bromide; by adding pyridine to an aq. soln. of the diaquotetramminosulphate acidified with acetic acid; or by adding alcohol to an ammoniacal soln. of the diaquotetramminosulphate, a process also employed by S. M. Jörgensen. The salt furnishes pale violet, rhombic plates. E. Rosenbohm gave  $-0.059 \times 10^{-6}$  mass unit for the magnetic susceptibility, and the magnetic properties were studied by W. Biltz, D. M. Bose, and L. C. Jackson. S. M. Jörgensen observed that the salt furnishes a red, aq. soln. with a feeble alkaline reaction; and the colour of the aq. soln., on standing, darkens, changing to brownish-violet and then to a brownish-black soln. of hexol-dodecaminosulphate; and with a warm 1:1-hydrochloric acid soln., chloroaquotetramminochloride is formed. J. V. Dubsy, A. Werner, and H. Frank observed that when a soln. in dil. acetic acid is treated with acetic anhydride, diol-octamminosulphate is formed.

S. M. Jörgensen<sup>8</sup> prepared **cobaltic chloropentamminosulphate**,  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$ , by triturating a mol of the chloride with 3 mols of conc. sulphuric acid, when hydrogen chloride is no longer evolved, adding water at  $70^\circ$ . The warm soln. deposits crystals of the *dihydrate* and of the anhydrous salt, the cold soln. yields nearly all dihydrate. A. Benrath obtained the anhydrous salt by seeding a soln. of the dihydrate with anhydrous salt; and the dihydrate, by rapidly cooling the hot-filtered soln. S. M. Jörgensen obtained the dihydrate as a lilac precipitate consisting of fine needles when a cold soln. of a mol of the chloride is treated with 8 to 10 mols of sulphuric acid. The anhydrous salt forms purple-brown, almost black, octahedral crystals, and it is considered to be the stable form because, according to S. M. Jörgensen, it is stable in air, over sulphuric acid, or when heated to  $100^\circ$ ; whereas the dihydrate forms purple-red, rhombic crystals which effloresce in air, or over sulphuric acid, and at  $100^\circ$ . S. M. Jörgensen said that the dihydrate, which he called the unstable form, dissolves more slowly in water, and is less soluble than the anhydrous salt: 100 grms. of water, at  $17.3^\circ$ , dissolve 0.769 grm. of the anhydrous salt, and 0.750 of the dihydrate. The subject was discussed by A. Benrath. F. Ephraim observed that a sat., aq. soln. of the anhydrous salt contains 0.0344 mol per litre at  $19^\circ$ ; and J. N. Brönsted

and A. Petersen, 0.029 mol per litre at 20°. A. Werner and A. Miolati found the mol. conductivity,  $\mu$ , of soln. with a mol of the salt in  $v$  litres, at 25°, to be :

$v$	:	:	64	128	256	512	1024	2048
$\mu$	:	:	218.8	240.5	253.7	266.9	276.1	284.8

K. Matsuno also made measurements of the mol. conductivity. S. M. Jörgensen found that a neutral aq. soln. of the salt gives a precipitate of silver chloride when it is warmed with silver nitrate, but not so with acidic soln.; barium hydroxide also forms a mixture of aquopentammino-chloride and hydroxide. A. Benrath measured the solubility of the salt in soln. of sulphuric acid, at 25°, and found the results indicated in Fig. 140. With 0 to 13 per cent. of  $H_2SO_4$ , the solid phase is

$[Co(NH_3)_5Cl]SO_4$ ; with 13 to 48 per cent.  $H_2SO_4$ , it is  $4[Co(NH_3)_5Cl]SO_4 \cdot 3H_2SO_4$ ; and with over 48 per cent.  $H_2SO_4$ , it is  $[Co(NH_3)_5Cl]SO_4 \cdot H_2SO_4$ . There is here no evidence of the formation of the **cobaltic chloropentamminosulphatohydrosulphate**,  $2[Co(NH_3)_5Cl]SO_4 \cdot H_2SO_4$ , reported by H. Biltz and E. Alefeld; nor of the **cobaltic chloropentamminosulphatotritetrahydrosulphate**,  $3[Co(NH_3)_5Cl]SO_4 \cdot 2H_2SO_4$ , reported by P. Job. The zone of stability of **cobaltic chloropentamminosulphatodihydrosulphate**,  $[Co(NH_3)_5Cl]SO_4 \cdot H_2SO_4$ , is indicated in A. Benrath's Fig. 140. The salt was prepared by J. Meyer and K. Gröhler, and its X-ray absorption spectrum was studied by F. de Boer. The zone of stability of **cobaltic chloropentamminosulphatohemitrihydrosulphate**,  $4[Co(NH_3)_5Cl]SO_4 \cdot 3H_2SO_4$ , is indicated in A. Benrath's Fig. 140. The salt was prepared by S. M. Jörgensen. F. M. Jäger found that the dark red needles are rhombic bipyramids with the axial ratios  $a : b : c = 0.9025 : 1 : 1.609$ ; the sp. gr. 1.769 at 17°; the mol. vol. 789.14; and the topic axial ratios  $\chi : \psi : \omega = 7.3649 : 8.1604 : 13.1300$ . Y. Shibata studied the absorption spectrum. S. M. Jörgensen said water decomposes the salt into its components; cold hydrochloric acid forms chloropentamminochloride; hydrofluosilicic acid, and hydrochloroplatinic acid give characteristic precipitates; and silver nitrate gives no precipitate in the cold, and an incomplete precipitation in hot soln. K. Matsuno studied the flocculating action of the salt on the hydrosol of arsenic sulphide. S. M. Jörgensen prepared **cobaltic chloropentamminobromosulphate**, in rectangular prisms; and also **cobaltic chloropentamminiodosulphate**,  $[Co(NH_3)_5Cl]_4(SO_4)_3(I_3)_2$ , in olive-green, rectangular plates.

A. Werner reported **cobaltic trans-chlorobisethylenediamineamminochlorosulphate**,  $[Co(NH_3)_2(en)_2Cl]Cl(HSO_4)$ , to be formed in ruby-red plates, by evaporating a mixture of the trans-nitroxylbisethylenediamineamminodithionate with conc. hydrochloric acid on a water-bath. The aq. soln. is strongly acidic. R. Vogel also prepared **cobaltic chlorobisethylenediaminepyridinesulphate**,  $[Co(en)_2pyCl]SO_4$ .

A. Werner and co-workers<sup>9</sup>—A. Klein, and A. Miolati—prepared **cobaltic cis-chloroaquatetramminosulphate**,  $[Co(NH_3)_4(H_2O)Cl]SO_4$ , by allowing a conc., aq. soln. of acidic dichlorotetramminosulphate to stand for some time; and S. M. Jörgensen, by treating a soln. of the corresponding chloride in dil. sulphuric or nitric acid with a 20 per cent. soln. of ammonium sulphate, or by triturating the chloride with conc. sulphuric acid, and diluting the mixture with 2 vols. of water. The salt furnishes violet, rhombic or rhomboidal plates. K. Matsuno found that the mol. conductivities of soln. with a mol of the salt in 400, 800, and 1600 litres of water, at 25°, are, respectively, 190.1, 218.7, and 259.2, so that aquation, attended by a transformation into diaquatetramminosulphate, occurs in aq. soln. A. Werner and A. Miolati measured the conductivity in dil. hydrochloric

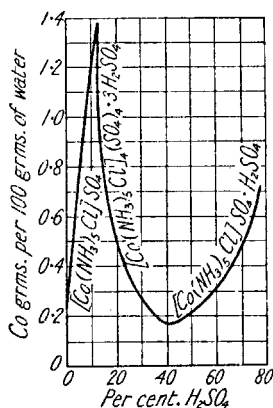


FIG. 140.—The Solubility of Chloropentamminosulphate in Sulphuric Acid.



acid soln. S. M. Jörgensen found that the salt dissolves in conc. sulphuric acid without forming hydrogen chloride, and hydrochloric acid precipitates from the soln. trans-dichlorotetramminochloride; and silver nitrate precipitates no silver chloride from the cold soln. K. Matsuno studied the flocculation of the hydrosol of arsenic sulphide by this salt.

A. Werner, and A. Werner and G. Tschernoff prepared **cobaltic chloroaquobisethylenediaminesulphate**,  $[\text{Co en}_2(\text{H}_2\text{O})\text{Cl}]\text{SO}_4 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ , by adding ammonium sulphate to a boiling soln. of the trans-dichlorobisethylenediaminechloride, and washing with cold water the salt which separates on cooling. The bluish-red crystals are sparingly soluble in cold water. A. Uspensky and K. Tschibisoff examined the absorption spectrum, and concluded that when the aq. soln. is warmed for a long time, aquation occurs, and a state of equilibrium with diaquochlorosulphate ensues. A. Werner observed that the addition of conc., aq. ammonia, followed by the addition of hydrobromic acid, converts the salt into chlorobisethylenediamineamminobromide; and F. M. Jäger and P. Koets studied the action of triaminotriethylamine on the salt. H. Fischlin obtained the *dextro-salt* and *levo-salt* by the action of 50 per cent. sulphuric acid on the optically-active bromides. The reddish-brown crystals of the *monohydrate*, so formed, lose water at  $40^\circ$ ; and the 0.1 per cent. aq. soln. have the sp. rotations  $[\alpha] = \pm 232^\circ$ . F. M. Jäger prepared **cobaltic chloroaquo-aphenanthrolinesulphate**. J. Meyer prepared cobaltic methylsulphatoaquotetramminomethylsulphate,  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{CH}_3\cdot\text{SO}_4)(\text{CH}_3\cdot\text{SO}_4)_2]$ .

S. M. Jörgensen<sup>10</sup> prepared **cobaltic chlorodiaquotriamminosulphate**,  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})\text{Cl}]\text{SO}_4$ , by allowing a cold, aq. soln. of acid dichloroaquotriammine sulphate to stand for some time; and A. Werner, by heating an aq. soln. of the acid sulphate on the water-bath and allowing the soln. to crystallize in vacuo. It separates in small, lustrous crystals, is almost insoluble in water, and can also be obtained by treating chlorodiaquotriamminochloride with sulphuric acid. The dark violet, rhombic plates were found by S. M. Jörgensen to be isomorphous with those of the chloroaquotetramminosulphate. The salt is sparingly soluble in cold water. K. Matsuno studied the absorption spectrum, and found that the mol. conductivities of soln. of a mol of the salt in 800, and 1600 litres of water, are, respectively, 259.2 and 462.9, at  $25^\circ$ . A. Werner found that the trituration of the salt with conc. hydrochloric acid forms the violet chloride; S. M. Jörgensen, that 1:1-hydrochloric acid converts it into dichloroaquotriamminochloride; A. Werner, that the soln. in dil. soda-lye, or in contact with potassium bromide and water, converts the sulphate into triol-hexamminosulphate; and K. Matsuno, that the salt is almost insoluble in alcohol. A. Werner, and K. Matsuno studied an isomeric, bluish-grey form of the salt obtained by adding alcohol to a cold, conc., aq. soln. of dichloroaquotriamminosulphate. A. R. Klein studied the action of water, acids, and alkali-lye.

A. Werner prepared **cobaltic cis-chlorotriaquodiamminosulphate**,  $[\text{Co}(\text{NH}_3)_2(\text{H}_2\text{O})_3\text{Cl}]\text{SO}_4 \cdot \text{H}_2\text{O}$ , by evaporating over sulphuric acid, an aq. soln. of dichlorodiaquodiamminosulphate, acidified with sulphuric acid. The indigo-blue, crystalline mass furnishes an indigo-blue aq. soln. whose absorption spectrum was studied by K. Matsuno, and found to correspond with that of cis-diaquobisethylenediaminochloride, but not with that of the trans-salt; he also found the mol. conductivity,  $\mu$ , of a soln. of a mol of the salt in  $v$  litres of water, at  $25^\circ$ , to be:

$v$ . . . . .	100	200	400	800	1600
$\mu$ . . . . .	184.2	222.3	267.6	332.7	412.3

S. M. Jörgensen<sup>11</sup> prepared **cobaltic bromopentamminosulphate**,  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ , along with the bromosulphate, by trituration of a mol of the bromochloride with 12 to 14 mols of cold, conc. sulphuric acid, diluting considerably with water after the escape of hydrochloric acid has ceased, and precipitating by addition of alcohol. If little water only be added, a blue-violet salt separates, which is most probably the acid sulphate. The normal sulphate may also be prepared from the bromobromide. It crystallizes in small, very dark violet octahedrons with brilliant lustre, which readily take up moisture and pass into the hydrated sulphate, a salt which probably contains 6 mols. of water of crystal-

lization. F. Ephraim found that a sat., aq. soln., at 20°, contains 0.0246 mol per litre. S. M. Jörgensen observed that if crystallized from dil. sulphuric acid, unstable **cobaltic bromopentamminohydrosulphate** is formed in violet needles, decomposed by water. F. Ephraim and W. Flügel said that a soln. of the salt gives no precipitate with potassium nitrilosulphonate. According to S. M. Jörgensen, if the soln. in dil. sulphuric acid be treated with a soln. of bromine and potassium iodide, unstable **cobaltic bromopentamminobromosulphate** is formed in reddish-brown plates; and with a soln. of iodine and potassium iodide, unstable **cobaltic bromopentamminiodosulphate**,  $[\text{Co}(\text{NH}_3)_5\text{Br}]_4(\text{SO}_4)_3(\text{I}_3)_2$ , is formed in black, rectangular plates.

A. Werner and A. Wolberg prepared **cobaltic cis-bromo-aquo-tetramminosulphate**,  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Br}]\text{SO}_4$ , in reddish- or bluish-violet crystals, by the addition of alcohol to a cold, aq. soln. of the corresponding bromide acidified with sulphuric acid; or by adding a mixture of alcohol and ether to a soln. of dibromotetramminosulphate. If the dry bromide be triturated with sulphuric acid (2 : 1), dark violet crystals of **cobaltic cis-bromo-aquo-tetramminobromosulphate**,  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Br}]_2(\text{SO}_4)\text{Br}_2$ , are formed.

F. Ephraim prepared **cobaltic iodopentamminosulphate**,  $[\text{Co}(\text{NH}_3)_5\text{I}]\text{SO}_4$ , by triturating the nitrate with sodium sulphate and a little water. A sat., aq. soln. contains 0.00529 mol per litre at 20°.

S. M. Jörgensen<sup>12</sup> prepared **cobaltic sulphatopentamminosulphate**,  $[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]_2\text{SO}_4 \cdot \text{H}_2\text{O}$ , by slowly adding alcohol to an aq. soln. of the hydrosulphate; and P. Job, by heating diaquopentamminosulphate, at 75°, until its weight is constant. It was also prepared by C. and M. Duval. According to S. M. Jörgensen, the violet-red, feebly dichroic needles cannot be re-crystallized from water alone, owing to aquation to the aquopentamminesulphate. A. Benrath observed that the neutral sulphato-sulphate does not occur as solid phase in the presence of sulphuric acid—*vide supra*, the aquopentamminosulphate—although it can be precipitated by alcohol from a soln. of the acid sulphate. F. Ephraim and W. Flügel said that a sat., aq. soln. contains 0.3464 gram-atom of cobalt per litre at 20°. P. Job found that at 0°, benzidine chloride precipitates only one-third of the contained  $\text{SO}_4$ -groups; but aquation occurs, so that there is a state of equilibrium between the sulphato-sulphate and the diaquo-sulphate—at 0°, about 5.5 per cent., and at 20°, about 11.3 per cent. of the diaquo-sulphate is formed. A. B. Lamb and J. W. Marden observed that a soln. of 0.0087 mol of the sulphato-sulphate per litre in 0.01M- $\text{H}_2\text{SO}_4$ , in 24 hrs. at 70°, suffers a 43.3 per cent. aquation. R. Schwarz and K. Tede studied the action of ultra-violet light in the transformation. For C. Duval's  $[\text{Co}(\text{NH}_3)_5(\text{SO}_4)']\text{SO}_4$ , *vide supra*, hydroxypentamminosulphate.

O. W. Gibbs and F. A. Genth, and S. M. Jörgensen prepared **cobaltic sulphatopentamminohydrosulphate**,  $[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]\text{HSO}_4 \cdot 2\text{H}_2\text{O}$ , in red prisms, by adding conc. sulphuric acid to soln. of the chloropentamminochloride or of the diaquopentamminosulphate. P. Job said that some aquopentamminosulphate is always formed by this process, and he recommended evaporating a soln. of the diaquo-sulphate in 2N- $\text{H}_2\text{SO}_4$ , in vacuo—the first crop of crystals furnishes the aquopentamminosulphate, and the next crop consists of the sulphato-hydrosulphate. P. Job and L. O. Tao observed that at ordinary temp., in contact with sulphuric acid of different concentrations, the solid phases are: (i) the diaquo-sulphate,  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]_2(\text{SO}_4)_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ ; (ii) the diaquo-sulphatohydrosulphate,  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]_7(\text{SO}_4)_{10}\text{HSO}_4$ ; and (iii) the sulphato-hydrosulphate,  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]_2(\text{SO}_4)\text{HSO}_4$ . The red prisms or plates of the hydrosulphate were found by S. M. Jörgensen to be dichroic. Observations on the crystals were made by J. D. Dana, and O. W. Gibbs and F. A. Genth. F. M. Jäger observed that the rhombic bipyramids have the axial ratios  $a : b : c = 0.7517 : 1 : 0.5364$ . F. M. Jäger found the sp. gr. to be 1.828 at 18°; the mol. vol., 204.04; and the topic axial ratios  $\chi : \psi : \omega = 5.9900 : 7.9689 : 4.2745$ . J. Petersen studied the

lowering of the f.p., and the mol. conductivity of aq. soln.; and E. Feytis, the magnetic susceptibility. The *dihydrate* loses 2 mols. of water at  $100^{\circ}$ ; and 100 grms. of cold water dissolve 4 grms. of the salt. P. Job observed no hydrolysis in cold, aq. soln. According to S. M. Jørgensen, and O. W. Gibbs and F. A. Genth, warming the salt with hydrochloric acid produces the chloro-chloride; dil. hydrochloric, hydrobromic, and nitric acids give precipitates after the addition of alcohol. The salt is almost insoluble in aq. ammonia; potassium iodide precipitates the iodide from aq. soln.; crystalline precipitates are obtained with sodium chloromercurate, sodium dithionate, potassium dichromate, hydrochloroplatinic acid, and hydrochloroauric acid; and ammonium oxalate, potassium cobalticyanide, and sodium pyrophosphates give no precipitates. K. Matsuno studied the constitution of these salts.

F. Ephraim and W. Flügel prepared **cobaltic sulphatopentamminochloride**,  $[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]\text{Cl}$ , by alcohol precipitation from a soln. of the acid sulphate in dil. hydrochloric acid. The rose-red precipitate has a bluish tinge. A sat., aq. soln. contains 0.2881 gram-atom of cobalt per litre. Barium chloride does not precipitate sulphate from the cold, aq. soln. The salt is insoluble in alcohol. It was also prepared by C. and M. Duval. By adding alcohol to a soln. of the acid sulphate in dil. hydrobromic acid, S. M. Jørgensen prepared **cobaltic sulphatopentamminobromide**,  $[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]\text{Br}$ , as a precipitate which crystallizes from conc., aq. soln. with the addition of hydrobromic acid (1 : 1), in violet-red, dichroic, rectangular plates. Measurements of the lowering of the f.p. were made by J. Petersen. A. Werner and A. Miolati also found that soln. with a mol of the salt in 32, 256, and 1024 litres, had the mol. conductivities 79.34, 101.6, and 114.2, respectively. Aquation thus occurs in dil., aq. soln. F. Ephraim and W. Flügel observed that the sat., aq. soln., at  $20^{\circ}$ , contains 0.0500 gram-atom of cobalt per litre. S. M. Jørgensen found that silver nitrate gives an immediate precipitate of silver bromide, but barium chloride gives a precipitate of barium sulphate only after the soln. has been warmed. F. Ephraim and W. Flügel prepared **cobaltic sulphatopentamminiodide**,  $[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]\text{I}$ , in small, red prisms, by treating the corresponding chloride with potassium iodide at  $50^{\circ}$ . The sat., aq. soln. contains 0.0371 gram-atom of cobalt at  $20^{\circ}$ . C. and M. Duval prepared cobaltic persulphatopentamminochloride.

P. Job prepared **cobaltic sulphatoaquotetramminosulphate**,  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{SO}_4)]_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ , in red crystals, from an aq. soln. of the acid sulphate. The *dihydrate* is only sparingly soluble in water, and the aq. soln. is not stable, for, by aquation, it forms diaquotetramminosulphate. J. Meyer and K. Gröhler obtained the *tetrahydrate* by exposing the sulphate, dried at  $110^{\circ}$ , in air; F. Ephraim and W. Flügel, by adding alcohol to a soln. of the carbonatotetramminonitrate in cold, dil. sulphuric acid; and W. Schramm, by adding alcohol to a soln. of the diaquotetramminosulphate in malonic acid. The tetrahydrate forms cherry-red, acicular crystals which are easily soluble in water; barium chloride precipitates barium sulphate from the cold, aq. soln., and there is another precipitation after the soln. has been boiled. The salt loses 4 mols of water at  $110^{\circ}$ , and decomposes at a higher temp. The anhydrous salt forms a bluish-violet soln. in water, which soon becomes cherry-red. The sat., aq. soln. has 0.1254 gram-atom of cobalt per litre at  $20^{\circ}$ . A soln. of cobaltic chloronitritotetramminochloride in cold, conc. sulphuric acid, when treated in the cold with absolute alcohol, furnishes the *dialcoholate*,  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{SO}_4)]_2\text{SO}_4 \cdot 2\text{C}_2\text{H}_5\text{OH}$ . This salt loses the alcohol at  $80^{\circ}$ , and when the residue is exposed to air, it forms the tetrahydrate. P. Job prepared **cobaltic sulphatoaquotetramminohydrosulphate**,  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{SO}_4)]\text{HSO}_4 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ , or  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{SO}_4)]_2\text{SO}_4 \cdot \text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ , in violet crystals, by evaporating a sulphuric acid (1 : 4) soln. of carbonatotetramminosulphate, or diaquotetramminosulphate on a water-bath, or in vacuo; and A. Benrath and K. Andreas, and K. Andreas, observed that when the diaquo-sulphate is in contact with over 80 per cent. sulphuric acid, it behaves like the pentamminosulphate, forming, at  $25^{\circ}$ , a

syrupe liquid which, at a low temp., furnishes crystals of the hydrosulphate,  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{SO}_4)]_2\text{SO}_4 \cdot \text{H}_2\text{SO}_4$ , *i.e.*  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{SO}_4)]\text{HSO}_4$ . P. Job studied the constitution by electrometric titration of the soln. with barium hydroxide, and the results indicate that an aquo-salt is formed which dissociates into a hydroxyl-salt and  $\text{H}^+$ -ions.

A. Werner prepared **cobaltic sulphatodiaquotriamminosulphate**,  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_2(\text{SO}_4)]_2\text{SO}_4 \cdot \text{H}_2\text{O}$ , by adding the requisite quantity of silver sulphate to a warm, conc. soln. of dichloroaquotriamminochloride and evaporating the filtrate from the silver chloride in vacuo. The residue is extracted with water, when the salt is left undissolved; by evaporating the soln. and again extracting with water, a further quantity of the insoluble salt is obtained. It is a reddish-violet powder, insoluble in water, but soluble in conc. hydrochloric, nitric, and sulphuric acids. When mixed with conc. hydrochloric acid, it yields chlorodiaquotriamminosulphate, and by the prolonged action of the acid, the dichloroaquochloride.

### *The CoA<sub>4</sub> or Tetrammine Family*

A. Werner<sup>13</sup> obtained **cobaltic cis-dichlorotetramminosulphate**,  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]_2\text{SO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ , in bluish-violet crystals, from a well-cooled soln. of the corresponding chloride in sulphuric acid (1:1). The salt is very sparingly soluble in water. There is no loss in weight over phosphorus pentoxide; but when heated to 70° or 80°, there is a loss of about 1.22 per cent., presumably owing to a partial decomposition of the salt.

E. Schmidt, and A. Werner and A. Klein prepared **cobaltic trans-dichlorotetramminohydrosulphate**,  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{HSO}_4$ , by treating the solid carbonato-tetramminochloride,  $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{Cl}$ , with conc. hydrochloric acid in a freezing mixture, dissolving the product in conc. sulphuric acid, and adding hydrochloric acid as long as a precipitate is formed; the mixture is then allowed to remain for a few days in a closed flask, and the precipitate collected and washed with alcohol and ether; it is easily purified by dissolving it in water and precipitating with dil. sulphuric acid. S. M. Jörgensen obtained it by the action of conc. sulphuric acid on the chloroaquotetramminochloride, or diaquotetramminosulphate. The salt was also prepared by A. Werner and A. Wolberg. It forms bright green needles, freely soluble in water. A. Werner and A. Miolati found that the conductivity of the aq. soln. increases with time, owing to the formation of chloroaquotetramminosulphate. Thus, the mol. conductivity of a soln. of a mol of the salt in 256 litres, at 25°, increases in 45 mins. from 372.7 to 426.5. A. Werner and A. Klein found that the salt is easily soluble in water, and has a strongly acidic reaction. With hydrochloric acid and chlorides, it yields a bright green, crystalline precipitate of dichlorotetramminochloride; it is decomposed by mercurous nitrate, potassium cyanide, and potassium ferrocyanide, and dissolves in conc. sulphuric acid, with a red coloration and the evolution of hydrogen chloride. It is more stable in aq. soln. than the other salts of the series, but the colour of the soln. gradually changes to blue, violet, becomes colourless, and finally red. When the conc., aq. solution is warmed, a precipitate of chloroaquotetramminosulphate,  $[\text{Co}(\text{NH}_3)_4\text{Cl}(\text{H}_2\text{O})]\text{SO}_4$ , is obtained in the form of lustrous, reddish-violet plates; this dissolves in conc. sulphuric acid, with a violet coloration, and when treated with conc. hydrochloric acid in aq. soln., yields chloroaquotetramminochloride. A. Werner, and T. S. Price and S. A. Brazier discussed the constitution of the double salts. A. Werner and A. Klein observed that **silver cobaltic dichlorotetramminosulphate**,  $[\text{Co}(\text{H}_2\text{O})_4\text{Cl}_2]\text{SO}_4\text{Ag}$ , is obtained as a flocculent, bright green precipitate by mixing soln. of eq. proportions of the hydrosulphate and silver nitrate at a low temp.; and **bismuth cobaltic dichlorotetramminosulphate**,  $\text{Bi}[\text{Co}(\text{NH}_3)_4\text{Cl}_2]_3(\text{SO}_4)_3$ , is similarly produced as a green, pulverulent precipitate.

A. Werner and R. Feenstra prepared **cobaltic trans-dichloroquaterpyridinehydrosulphate**,  $[\text{Co}(\text{C}_5\text{H}_5\text{N})_4\text{Cl}_2]\text{HSO}_4 \cdot 2\text{H}_2\text{O}$ , in green plates and needles, by the action of dil.

sulphuric acid on an aq. soln. of the chloride, and re-crystallization from aq. soln. at 50°. A. Werner prepared **cobaltic cis-dichlorobisethylenediaminesulphate**,  $[\text{Co en}_2\text{Cl}_2]\text{SO}_4 \cdot 2\text{H}_2\text{O}$ , in small, reddish-violet needles, by treating a conc., aq. soln. of the chloride with ammonium sulphate; or by evaporating the mother-liquor obtained in the preparation of chloroaquobisethylenediaminesulphate. A. Gordienko studied the absorption spectrum. A. Werner and G. Tschernoff obtained the *dextro-salt*, and the *levo-salt* by the action of ammonium sulphate on sat., aq. soln. of the corresponding chlorides. The sp. rotation of a 0.25 per cent. aq. soln. of the dextro-salt is  $[\alpha] = 180^\circ$ , and the levo-salt,  $-182^\circ$ . A. Werner, and L. Cohn prepared **cobaltic trans-dichlorobisethylenediaminehydrosulphate**,  $[\text{Co en}_2\text{Cl}_2]\text{HSO}_4$ , as a green, crystalline precipitate, by the action of sulphuric acid on an aq. soln. of the chloride, and re-crystallization from water acidulated with sulphuric acid. If a well-cooled, aq. soln. be treated with silver nitrate, green plates of **silver cobaltic dichlorobisethylenediaminesulphate**,  $[\text{Co en}_2\text{Cl}_2]\text{SO}_4 \cdot 2\text{AgNO}_3$ , are formed. The salt is stable, and sparingly soluble in water. Its constitution was discussed by A. Werner, and T. S. Price and S. A. Brazier. A. Werner and A. Frölich found that **trans-cobaltic dichlorobispropylenediaminehydrosulphate**,  $[\text{Co pn}_2\text{Cl}_2]\text{HSO}_4 \cdot 2\text{H}_2\text{O}$ , is formed in green, soluble needles, from a soln. of the corresponding chloride in conc. sulphuric acid. If the acid sulphate be treated with silver nitrate, there are formed malachite-green scales of a complex with silver nitrate. A. Werner and F. Chaussy obtained **cobaltic trans-dichloroethylenediaminediamminohydrosulphate**,  $[\text{Co}(\text{NH}_3)_2\text{enCl}_2]\text{HSO}_4 \cdot \text{H}_2\text{O}$ , as a green to brown precipitate, by adding 1:1-sulphuric acid to a conc., aq. soln. of the corresponding chloride at  $-4^\circ$ .

S. M. Jörgensen, and A. Werner prepared **cobaltic dichloroaquotriamminohydrosulphate**,  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})\text{Cl}_2]\text{HSO}_4$ , by mixing the dichloroaquotriamminochloride to a thin paste with a cool mixture of conc. sulphuric acid (2 vols.) and conc. hydrochloric acid (1 vol.), and after the mixture has remained for 1 hr., spreading the paste on a porous plate. This operation is repeated three times, and the product then washed with alcohol until free from acid, and dried over sulphuric acid. It is a greyish-green, crystalline powder, and dissolves fairly easily in water, yielding a green solution which quickly changes to indigo-blue; the solution has an acid reaction. It is obtained in black, lustrous, prismatic crystals by adding conc. sulphuric acid to the cold, conc., aq. soln. and evaporating the clear liquid in vacuo over sulphuric acid. S. M. Jörgensen found that 100 grms. of water dissolve 16 to 20 grms. of the salt. Aquation occurs in aq. soln. to form chlorodiaquotriamminosulphate, which, according to A. Werner, has precipitated this product from the blue soln. by alcohol. The double salt, **silver cobaltic dichloroaquotriamminosulphate**,  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})\text{Cl}_2]\text{AgSO}_4$ , is produced by thoroughly mixing the acid sulphate with a small quantity of silver nitrate soln., and washing the product with absolute alcohol. It is a grass-green powder which quickly decomposes and darkens, and it is decomposed by water, with the separation of silver chloride.

A. Werner prepared **cobaltic dichlorodiaquodiamminohydrosulphate**,  $[\text{Co}(\text{NH}_3)_2(\text{H}_2\text{O})_2\text{Cl}_2]\text{HSO}_4$ , by adding potassium tetranitritodiamminocobaltate (3 grms.) to a mixture of equal vols. of sulphuric and hydrochloric acids, cooled with ice and salt, and allowing the mixture to remain some hours in the freezing mixture. After 24 hrs., the product is washed with alcohol and ether, dissolved in ice-cold water, and precipitated with sulphuric acid. A. Werner and R. Feenstra obtained it from ammonium tetranitritodiamminocobaltate. The salt crystallizes in lustrous, malachite-green needles, soluble in water, to form a green soln. with an acidic reaction, and which quickly changes to a blue soln. which, with alcohol, gives a precipitate of chlorotriaquodiamminosulphate. The same product is obtained by slowly evaporating the soln. K. Matsuno showed that the aq. soln. probably contains different aquo-salts in equilibrium; he studied the absorption spectrum, and the flocculating action of the salt on the hydrosol of arsenic sulphide.

A. Werner and A. Wolberg prepared **cobaltic dibromotetramminosulphate**,  $[\text{Co}(\text{NH}_3)_4\text{Br}_2]\text{SO}_4$ , in small, green crystals, by the action of sulphuric acid on the corresponding chloride. The salt is freely soluble in water, and it rapidly changes in aq. soln., to form the aquo-salt.

A. Werner and G. Tschernoff prepared optically active **cobaltic cis-bromochlorobisethylenediaminesulphate**,  $[\text{Co en}_2\text{Cl Br}]\text{SO}_4 \cdot \text{H}_2\text{O}$ , as a pale violet, crystalline powder,

by treating the corresponding nitrate with conc. sulphuric acid. The sp. rotation of a dil. soln. of the *dextro-salt* is  $[\alpha] = 144^\circ$ , and of the *levo-salt*,  $-148^\circ$ . J. C. Duff prepared **cobaltic sulphatobisethylenediaminebromide**,  $[\text{Co en}_2(\text{SO}_4)]\text{Br} \cdot \text{H}_2\text{O}$ , by evaporating a soln. of carbonatobisethylenediaminebromide treated with an eq. proportion of  $\text{N} \cdot \text{H}_2\text{SO}_4$ . These salts were studied by P. Job, and F. Ephraim and W. Flügel. The dark red crystals lose their water of hydration in air; barium chloride precipitates barium sulphate from the aq. soln. only after it has been heated. The mol. conductivity,  $\mu$ , of a soln. of a mol of the salt in  $v$  litres, at  $25^\circ$ , is:

$v$	.	.	.	32	64	128	256	512	1024
$\mu$	.	.	.	90.4	98.56	106.9	114.0	119.7	125.2

### *Complexes with Two or More Cobalt Atoms*

The nature of the products obtained by the slow oxidation of ammoniacal soln. of cobaltous sulphate, as well as of *G. Vortmann's salt*,<sup>14</sup> or *cobaltic fuscousulphate*, have been discussed in connection with *cobaltic melanochloride*, etc.; and it was prepared by C. Schwenk. E. Frémy, and G. Vortmann reported a brown salt,  $\text{Co}_2(\text{NH}_3)_8(\text{OH})_2(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$ , whose constitution has not been determined.

E. Frémy prepared what has since been shown to be **cobaltic peroxo-decamminodisulphate**,  $[(\text{NH}_3)_5\text{Co}-\text{O}_2-\text{Co}(\text{NH}_3)_5](\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$ , by the slow oxidation of an ammoniacal soln. of cobaltous sulphate. The olive-brown prisms were considered to be the *trihydrate*, G. Vortmann said the *tetrahydrate*. The salt is soluble in water, but the soln. decomposes, with the evolution of oxygen; the soln. in aq. ammonia is stable. It gives reactions similar to those of the nitrate. According to G. Vortmann, **cobaltic peroxo-decamminohydrosulphate**,  $[(\text{NH}_3)_5\text{Co}-\text{O}_2-\text{Co}(\text{NH}_3)_5](\text{HSO}_4)_4 \cdot \text{H}_2\text{O}$ , is obtained by adding the sulphate to sulphuric acid 1 : 1. The cinnabar-red precipitate is the *monohydrate*. If the sulphate be added to a mixture of equal vols of sulphuric acid, water, and alcohol, the *pentahydrate* is formed. The salts are stable in air at  $13^\circ$ , but at  $20^\circ$ , they become green, owing to decomposition. The aq. soln. also decomposes with the deposition of cobaltous sulphate and the evolution of oxygen. If the sulphate be treated with conc. hydrochloric acid, a brownish-violet precipitate of **cobaltic peroxo-decammino-hydrochlorosulphate**,  $[(\text{NH}_3)_5\text{Co}-\text{O}_2-\text{Co}(\text{NH}_3)_5](\text{SO}_4)\text{Cl}_2 \cdot 4\text{HCl} \cdot \text{H}_2\text{O}$ , is produced.

L. Maquenne obtained a salt which was afterwards shown to be **cobaltic peroxo-decamminohemipentasulphate**,  $[(\text{NH}_3)_5\text{Co}-\text{O}_2-\text{Co}(\text{NH}_3)_5]_2(\text{SO}_4)_5 \cdot 8\text{H}_2\text{O}$ , by passing ozonized oxygen through an ammoniacal soln. of cobaltous sulphate, when the colour changes to brown, then green, and finally deposits dark green crystals on the sides of the containing vessel. He said:

The salt can be easily obtained by passing a rapid current of air through a mixture of 100 c.c. ammonia with 10 c.c. of a sat. soln. of cobalt sulphate for about 2 hours. The precipitated crystals are collected, dried rapidly between filter-paper, and thrown, in small portions at a time, into 25 c.c. of a cooled mixture of equal vols. of sulphuric acid, alcohol, and water, when the brown substance becomes rose-coloured. On adding an excess of chlorine-water, the rose-coloured compound becomes green, and the liquid, if heated to boiling, and left to cool, deposits prismatic crystals which are sometimes as much as 5 mm. long, and can be obtained larger by re-crystallization from dil. (5 per cent.) sulphuric acid.

G. Vortmann found that the same product is obtained by re-crystallizing the acid sulphate from water; or, by treating the tetranitrate with cold 1 : 1-sulphuric acid for some hours, diluting with water and warming the mixture for complete dissolution. The acid nitratosulphate separates out on cooling, and when this product is re-crystallized from water it yields green crystals of the hemipentasulphate. L. Maquenne said that the crystals are dark green, almost black, quadratic prisms; they are but slightly soluble in water, by which they are decomposed with evolution of oxygen, but they dissolve easily in dilute acids without sensible decomposition, even at  $100^\circ$ , if the operation is conducted rapidly. By prolonged ebullition with acids, this compound is converted into a rosecobalt salt. It is entirely decomposed by the fixed alkalies, with evolution of oxygen and precipitation of black cobaltic oxide. Conc. hydrochloric acid converts the sulphate into the correspond-

ing chloride. According to G. Vortmann, the acid salt prepared by L. Maquenne is a hydrosulphate; and the former obtained **cobaltic peroxo-decamminosulphato-dihydrosulphate**,  $[(\text{NH}_3)_5\text{Co}-\text{O}_2-\text{Co}(\text{NH}_3)_5]_2(\text{SO}_4)_5 \cdot 2\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ , by treating the tetrasulphate with a cold, sat. soln. of potassium permanganate and sulphuric acid (1 : 5); when the red colour has disappeared, the soln. is boiled. The dark bluish-green prisms are almost black, they lose water at  $110^\circ$ , and at  $130^\circ$  are decomposed. When re-crystallized from water, the normal sulphate is produced, and when re-crystallized from dil. sulphuric acid, **cobaltic peroxo-decamminosulphatomonohydrosulphate**,  $[(\text{NH}_3)_5\text{Co}-\text{O}_2-\text{Co}(\text{NH}_3)_5]_2(\text{SO}_4)_5 \cdot \text{H}_2\text{SO}_4$ , is produced. When the chloride of this series of salts is treated with 1 : 1-sulphuric acid, grass-green crystals of **cobaltic peroxo-decamminochlorosulphate**,  $[(\text{NH}_3)_5\text{Co}-\text{O}_2-\text{Co}(\text{NH}_3)_5](\text{SO}_4)_2\text{Cl} \cdot 3\text{H}_2\text{O}$ , are formed.

A. Werner prepared **cobaltic  $\mu$ -amino-decamminosulphate**,  $[(\text{NH}_3)_5\text{Co}-\text{NH}_2 \cdots \text{Co}(\text{NH}_3)_5]_2(\text{SO}_4)_5 \cdot 6\text{H}_2\text{O}$ , by treating a soln. of the bromide with a conc., aq. soln. of sodium sulphate. The rose-red needles are soluble in water; they are stable at  $85^\circ$ , but are slowly decomposed at  $100^\circ$ . A. Werner and F. Salzer prepared **cobaltic chloroaquo- $\mu$ -amino-octamminosulphate**,  $[(\text{H}_2\text{O})(\text{NH}_3)_4\text{Co}-\text{NH}_2 \cdots \text{Co}(\text{NH}_3)_4\text{Cl}](\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ , by treating a freshly-prepared soln. of the chloride with dil. sulphuric acid. The reddish-violet crystals are insoluble in water; at  $105^\circ$ , the water of aquation is given off. A. Werner prepared the corresponding **cobaltic bromoaquo- $\mu$ -amino-octamminosulphate**,  $[(\text{H}_2\text{O})(\text{NH}_3)_4\text{Co}-\text{NH}_2 \cdots \text{Co}(\text{NH}_3)_4\text{Br}](\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ , by treating an ice-cold soln. of the bromide with 1 : 1-sulphuric acid. The dark brown crystals are almost insoluble in water.

A. Werner and A. Baselli prepared **cobaltic sulphato- $\mu$ -amino-octamminohydrosulphate**,  $[(\text{NH}_3)_4\text{Co}=(\text{NH}_2)(\text{SO}_4) \cdots \text{Co}(\text{NH}_3)_4\text{H}(\text{SO}_4)_2]$ , by heating the corresponding chloride with conc. hydrochloric acid, on a water-bath, as long as hydrogen chloride is evolved, and then pouring the mixture into ice-cold water. A. Werner and F. Salzer recommended heating 3 grms. of  $\mu$ -amino-ol-octamminochloride with 10 c.c. of water and 2 c.c. of conc. sulphuric acid until a clear, violet soln. is obtained; purple-violet, prismatic leaflets are deposited on cooling. The salt can be re-crystallized from dil. sulphuric acid. The salt is almost insoluble in water, and the soln. reacts acidic to litmus. A. Werner, F. Steinitzer and K. Rücker obtained **cobaltic sulphato- $\mu$ -amino-octamminochloride**,  $[(\text{NH}_3)_4\text{Co}=(\text{NH}_2)(\text{SO}_4) \cdots \text{Co}(\text{NH}_3)_4]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ , by triturating the corresponding nitrate with hydrochloric acid. The violet crystals can be re-crystallized from water. Y. Shibata studied the absorption spectrum. A. Werner and co-workers added that when this salt is heated for 6 hours at  $110^\circ$ , it loses a mol. of hydrogen chloride, and is converted into the sulphato-chloride, a small quantity of imido-octamminedicobaltsulphate being formed at the same time. A. Werner and A. Baselli prepared **cobaltic sulphato- $\mu$ -amino-octamminobromide**,  $[(\text{NH}_3)_4\text{Co}=(\text{NH}_2)(\text{SO}_4) \cdots \text{Co}(\text{NH}_3)_4]\text{Br}_3 \cdot \text{H}_2\text{O}$ , by treating the nitrate or hydrosulphate with hydrobromic acid; and A. Werner, by adding hydrobromic acid to a soln. of the hydrosulphate; and by boiling  $\mu$ -amino-ol-octamminobromide with water and dil. sulphuric acid, and mixing the cold soln. with hydrobromic acid. The silky, violet needles lose no water over sulphuric acid, but the salt becomes anhydrous at  $110^\circ$ . A. Werner and A. Baselli added sodium or potassium iodide to a soln. of the chloronitrate, and obtained a dark brown, crystalline precipitate of **cobaltic sulphato- $\mu$ -amino-octamminoiodide**,  $[(\text{NH}_3)_4\text{Co}=(\text{NH}_2)(\text{SO}_4) \cdots \text{Co}(\text{NH}_3)_4]\text{I}_3$ . A. Werner prepared **cobaltic sulphato- $\mu$ -aminoquaterethylenediaminebromide**,  $[\text{en}_2\text{Co}=(\text{NH}_2)(\text{SO}_4) \cdots \text{Co en}_2]\text{Br}_3$ , as a red, crystalline powder, by treating the corresponding thiocyanate, or nitrate with ammonium bromide.

A. Werner prepared **cobaltic diol-octamminosulphate**,  $[(\text{NH}_3)_4 \cdots \text{Co}(\text{OH})_2 \cdots \text{Co}(\text{NH}_3)_4](\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ , by heating cobaltic hydroxyaquotetramminosulphate, between  $100^\circ$  and  $110^\circ$ , until its weight is constant; and H. Frank, by heating that salt with ten times its weight of acetic anhydride, or by treating the corresponding chloride with sodium sulphate. The violet-red needles are sparingly soluble in

water; and, according to H. Frank, the salt is not changed by warming it with acetic anhydride. A. Werner also prepared **cobaltic diaquo-diol-hexamminosulphate**,  $[(\text{H}_2\text{O})(\text{NH}_3)_3\text{Co} \cdots (\text{OH})_2 \cdots \text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})](\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$ , by digesting an aq. soln. of dinitrato-diol-hexamminonitrate for 24 hrs. and then adding sodium sulphate. The bluish-violet crystals are sparingly soluble in water.

According to A. Werner, when cobaltic melanochloride (*q.v.*) is prepared by the exposure of ammoniacal cobalt chloride solns. to the air, at temps. below  $5^\circ$ , and then worked up with silver nitrate, it yields a brownish-black nitrate in addition to the salts of the  $\mu$ -amino-peroxo-ol-hexammines. From this brownish-black nitrate, **cobaltic hydroxyammino-peroxo-ol-hexamminosulphate**,  $[(\text{OH})(\text{NH}_3)_3\text{Co} = (\text{OH})(\text{O}_2) \cdots \text{Co}(\text{NH}_3)_3(\text{OH})_2(\text{SO}_4)_3]$ , is obtained by treating it with an excess of ammonium bromide. The bromide is dissolved in dil. acetic acid and treated with ammonium sulphate. The dark green salt which separates is boiled many times with dil. acetic acid, or the double salt with ammonium sulphate is dissolved in water acidulated with acetic acid, and allowed to crystallize. The brownish-black crystals dissolve sparingly in water, and the soln. has an alkaline reaction. The salt is readily soluble in dil. acetic acid. On heating the salt with conc. sulphuric acid, it is decomposed with evolution of oxygen and nitrogen, the volumes of these gases obtained showing that the compound contains a peroxo-group and tervalent and quadrivalent cobalt. The double salt, **ammonium cobaltic hydroxyammino-peroxo-ol-hexammino-sulphate**,  $[(\text{OH})(\text{NH}_3)_3\text{Co} = (\text{OH})(\text{O}_2) \cdots \text{Co}(\text{NH}_3)_3(\text{OH})_2(\text{SO}_4)_2\text{NH}_4 \cdot \text{H}_2\text{O}]$ , is precipitated when glacial acetic acid is added to a soln. of the nitrate saturated with ammonium sulphate. The black crystals are readily soluble in water; and if an acetic acid soln. of the salt is boiled, and cooled, the normal sulphate is deposited.

A. Werner and co-workers—F. Beddo, and A. Grün—prepared **cobaltic  $\mu$ -amino-peroxo-octamminosulphate**,  $[(\text{NH}_3)_4\text{Co} = (\text{NH}_2)(\text{O}_2) \cdots \text{Co}(\text{NH}_3)_4](\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ , by treating an aq. soln. of another salt of the series with dil. sulphuric acid. The greenish-grey, crystalline precipitate is insoluble in water; but it forms a yellowish-brown soln. with conc. sulphuric acid, and when this soln. is diluted with water, the original salt is recovered unchanged. When the crystals are triturated with conc. hydrochloric or nitric acids, the corresponding chloride or nitrate is formed.

A. Werner and A. Baselli prepared **cobaltic  $\mu$ -amino-ol-octamminosulphate**,  $[(\text{NH}_3)_4\text{Co} = (\text{NH}_2)(\text{OH}) \cdots \text{Co}(\text{NH}_3)_4](\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ , by adding sulphuric acid to a sat., aq. soln. of the corresponding chloride; or by shaking the chloride with an acetic acid soln. of silver nitrate, and treating the filtrate with sulphuric acid. The garnet-red or brownish-red, prismatic crystals are insoluble in water. They lose their water of hydration over phosphorus pentoxide; and when heated with conc. sulphuric acid, cobaltous sulphate is formed, and nitrogen is evolved.

A. Werner prepared **cobaltic triol-hexamminosulphate**,  $[(\text{NH}_3)_3\text{Co} \cdots (\text{OH})_3 \cdots \text{Co}(\text{NH}_3)_3](\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$ , by the action of soda-lye on chlorodiaquotriamminosulphate; or by treating the corresponding chloride or bromide with a cold, sat. soln. of sodium sulphate. The red, scaly crystals quickly lose 5 mols. of water when confined over phosphorus pentoxide, and the remaining mol. of water is lost more slowly. All the water is expelled at  $70^\circ$ , and the salt decomposes at  $100^\circ$ . The salt is sparingly soluble in cold water; and when treated with nitric acid (1 : 1), the diol-group is nitrated to form  $[\text{Co}_2(\text{NH}_3)_6(\text{OH})_2(\text{NO}_3)_2(\text{NO}_3)_2]$ . A. Werner noted that the mother-liquor obtained in preparing cobaltic triol-hexamminosulphate deposits, on cooling, a dark green, crystalline precipitate of **cobaltic hexol-hexamminosulphate**,  $[\text{NH}_3)_3\text{Co} \equiv (\text{OH})_3 \cdots \text{Co} \cdots (\text{OH})_3 \equiv \text{Co}(\text{NH}_3)_2](\text{SO}_4)_3]$ .

A. Werner and G. Jantsch prepared **cobaltic diaquo-tetrol-quaterethylenediaminesulphate**,  $[\text{en}_2\text{Co} = (\text{OH})_2 \cdots \text{Co}(\text{H}_2\text{O})_2 \cdots (\text{OH})_2 = \text{Co en}_2](\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ , by treating the corresponding chloride (*q.v.*) with sodium sulphate, when microscopic, red needles of the *pentahydrate* are formed. Again, a soln. of cobalt sulphate containing ethylenediamine, deposits, on exposure to the air, the sulphate in the form of red



needles. It cannot be re-crystallized, being sparingly soluble in water, but when treated with barium chloride and then with sodium sulphate, the *heptahydrate* is formed. Both salts are almost insoluble in water, and lose their water of hydration over phosphorus pentoxide.

S. M. Jørgensen<sup>15</sup> prepared **cobaltic hexol-dodecammino-sulphate**,  $[\text{Co}\{(\text{OH}_2 = \text{Co}(\text{NH}_3)_4\}_3(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ , by keeping an ammoniacal or an alkaline soln. of chloroaquotetramminosulphate in the cold; by treating an aq. soln. of the corresponding chloride with ammonium sulphate; and by the action of  $N\text{-NH}_4\text{OH}$  on diaquotetramminosulphate. A. Werner and E. Berl prepared it by heating dibromotetramminobromide with a little water until bromine is evolved, and treating the soln. of the product with a soln. of ammonium sulphate; it is also obtained by adding pyridine to a hot, dilute, acetic acid soln. of diaquo-tetramminosulphate. According to A. Werner and E. Berl, the dark brownish-violet or black, tabular crystals, when washed with water, alcohol, and ether, furnish the *enneahydrate*; if dried over calcium chloride, the *hexahydrate*; and over sulphuric acid, or at 98°, the *tetrahydrate*. The salt is broken down by hydrochloric acid—*vide supra*, the chloride; boiling, dil. sulphuric acid liberates oxygen; and hot, conc. sulphuric acid liberates oxygen and nitrogen. According to S. M. Jørgensen, the salt is sparingly soluble in water, and the brownish-violet, aq. soln. gives quantitative precipitates with sodium chloromercurate, potassium chromate, and hydrochloroplatinic acid.

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## § 25. Cobaltous Carbonate

A. Weisbach<sup>1</sup> described a mineral which occurs sparingly with roselite,  $(\text{Co}, \text{Mg}, \text{Ca})_3(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$ , at Schneeberg, Saxony, and he called it **sphaerocobaltite**. Analyses reported by A. Weisbach, and A. A. Ferro correspond with **cobaltous carbonate**,  $\text{CoCO}_3$ . A. A. Ferro found the mineral at Libiola, Italy; M. Baccaredda, at Liguria, Italy; and A. Schoep, at Katanga, Belgian Congo. H. de Sénarmont found 0.13 per cent. of cobalt associated with the copper carbonate at Przibram. J. C. Booth described a rose-red incrustation on the serpentine at a copper mine near Finksburg, Maryland; he regarded it as a hydrated cobaltous carbonate, and he called it **remingtonite**—after E. Remington. E. V. Shannon showed that remingtonite is not a carbonate, but a kind of serpentine coloured with cobalt. The optical data by E. S. Larsen for a variety from California, are taken to refer to an anhydrous carbonate of the rhombohedral or trigonal series—possibly a cobaltiferous smithsonite,  $\text{ZnCO}_3$ .

H. de Sénarmont prepared cobaltous carbonate by heating a soln. of cobalt chloride with calcium carbonate, in a sealed tube, at  $150^\circ$  for 18 hrs.; or a soln. of sodium hydrocarbonate, saturated with carbon dioxide, mixed with cobalt chloride, in a sealed tube, at  $140^\circ$ . A. Barth obtained a theoretical yield by electrolyzing a soln. of a halide of the alkalis or alkaline earths with a cobalt anode whilst carbon dioxide is passing through the soln. B. Bruzs could not

prepare the anhydrous carbonate by heating one of the hydrates in carbon dioxide.

H. St. C. Deville found that precipitated cobalt carbonate dissolves in a soln. of ammonium hydrocarbonate, and deposits tabular crystals of a double salt which gradually passes into a violet-red powder of the *tritadihydrate*,  $\text{CoCO}_3 \cdot \frac{2}{3}\text{H}_2\text{O}$ ; the same hydrate is formed when crystals of the hexahydrate are allowed to stand in the mother-liquor at  $20^\circ$  to  $25^\circ$ . G. L. Clark and H. K. Buckner obtained the anhydrous carbonate by this procedure. H. St. C. Deville also obtained the *hexahydrate*,  $\text{CoCO}_3 \cdot 6\text{H}_2\text{O}$ , by keeping, in a sealed tube, a mixture of cobalt nitrate and of a soln. of sodium hydrocarbonate saturated with carbon dioxide; an amorphous precipitate is at first produced, but when exposed to a winter's cold, microscopic prisms appear. This hydrate does not change on exposure to air, but at a higher temp., passes into the tritadihydrate; and at  $100^\circ$ , both carbon dioxide and water are evolved. G. Cesaro said that the crystal plates are doubly refracting, and resemble those of stilbite (monoclinic).

Sphærocobaltite, anhydrous cobalt carbonate, occurs in small, spherical masses with a crystalline surface and a concentric, radiated structure. B. Üebler observed tree-like formations in slow precipitations. The colour is rose-red, altering superficially to a velvety black. The streak is peach-blossom red. H. de Sénarmont said that the artificial carbonate occurs as a red powder consisting of microscopic rhombohedra belonging to the trigonal system. A. Johnsen observed that the crystals are isomorphous with the magnesium, manganous, and ferrous carbonates. P. P. Ewald and C. Hermann referred the space-lattice of the rhombohedral crystals to that of the calcite type. A. Ferrari and C. Colla said that there are 4 mols. of  $\text{CoCO}_3$  per unit cell, which has  $a=5.91 \text{ \AA}$ , and  $\alpha=103^\circ 22'$ . M. Baccaredda gave for sphærocobaltite,  $a=5.72 \text{ \AA}$ , and  $\alpha=48^\circ 14'$ , and 2 mols. of  $\text{CoCO}_3$  per unit cell. A. Weisbach gave 4.02 to 4.13 for the sp. gr.; A. Lemke and W. Biltz, 4.124; and I. I. Saslawsky gave 4.0 to 4.13; and the value calculated by A. Ferrari and C. Colla from the lattice constants, is 4.24; and M. Baccaredda, 4.10. A. Lemke and W. Biltz, and I. I. Saslawsky discussed the vol. contraction which occurs during the formation of the salt from its elements. According to A. Weisbach, the hardness is 4.0. According to C. Winkler, the salt loses carbon dioxide when heated in air, and black cobaltous oxide is formed. J. Krustinsons, A. A. Noyes and W. E. Vaughan studied the subject. F. de Carli gave for the dissociation press.,  $p$  mm.:

	220°	258°	280°	318°
$p$ . . . .	63.42	269.10	389.80	760.00

The calculated heat of dissociation is  $\text{CoO} + \text{CO}_2 = \text{CoCO}_3 + 7.980 \text{ Cals.}$  The thermal decomposition was studied by B. Bruzs, and measurements of the rates of dissociation make it appear as if the decomposition occurs in two stages:  $2\text{CoCO}_3 = \text{CoO} \cdot \text{CoCO}_3 + \text{CO}_2$ , followed by  $\text{CoO} \cdot \text{CoCO}_3 = 2\text{CoO} + \text{CO}_2$ . M. le Blanc and E. Möbius observed that in a high vacuum, the thermal decomposition furnishes pure cobaltous oxide. F. de Carli calculated for the heat of formation ( $\text{Co}, \text{C}, \frac{1}{2}\text{O}_2$ )  $=163.13$  to  $173.31 \text{ Cals.}$ ;  $[\text{Co}(\text{OH})_2, \text{CO}_2 \text{ aq.}] = 10 \text{ Cals.}$ ; and  $(\text{CoO}, \text{CO}_2) = 7.98 \text{ Cals.}$  E. Bertrand found that the birefringence is negative. There is a marked pleochroism—rose-red parallel to the principal axes, and violet-red when perpendicular to those axes. M. Kimura and M. Takewaki studied the transparency of the salt to ultra-violet rays. M. Trautz observed no crystalloluminescence, or triboluminescence. W. A. D. Rudge observed the spluttering of carbonate in the negative discharge. G. Wiedemann said that the carbonate is paramagnetic. When heated in the presence of oxygen, the carbonate is decomposed and cobaltous oxide is formed (*q.v.*). R. Bernard and P. Job studied the oxidation of alkaline soln. in air. J. J. Berzelius observed that the carbonate is attacked by water, to form a basic carbonate. J. von Essen found that after cobalt carbonate had stood in contact with water at  $15^\circ$  for a month, 0.0273 grm. per litre passed into

soln., and at 100°, 0.0293 grm. per litre dissolved. Both W. J. Russell, and F. de Carli noted that cobalt carbonate is hydrolyzed by contact with water. G. Gore observed that liquefied hydrogen fluoride dissolves the carbonate with effervescence; and with liquid hydrogen chloride no perceptible evolution of gas occurs, and the liquid becomes a greenish-blue; whilst the residue becomes rose-red in air, and dissolves in dil. hydrochloric acid, without the evolution of gas. H. de Sénarmont observed that the crystalline powder is not attacked by conc. hydrochloric or nitric acids in the cold, and C. Winkler said that the action is very small, but when warmed, the carbonate dissolves, with the evolution of carbon dioxide. M. Kwiatnowsky recommended the carbonate as a reagent for detecting free hydrochloric acid in gastric juices. According to J. Gibson, when sodium carbonate is added in large excess to a soln. of a cobaltous salt, and the mixture shaken with a sufficient quantity of bromine, the whole of the precipitated cobaltous carbonate dissolves to a dark green soln., stable at ordinary temp., cobaltic oxide being precipitated on the addition of an aq. soln. of alkali hydroxide. If this green liquid is acidified with sulphurous acid, and the decolorized soln. be then oxidized, a red-coloured soln. is produced which absorbs oxygen from the air, and again becomes green. C. Dufraisse and D. Nakae studied the catalytic effect on the oxidation of soln. of sodium sulphite. G. Gore, and E. C. Franklin and C. A. Kraus found cobalt carbonate to be insoluble in liquid ammonia, and G. L. Clark, and G. L. Clark and H. K. Buckner reported that cobalt carbonate does not absorb dry ammonia; but it does dissolve in conc., aq. ammonia, and when the soln. is evaporated in vacuo, an unstable, hydrated **cobaltous amminocarbonate**,  $\text{CoCO}_3 \cdot 3\text{NH}_3 \cdot 4\text{H}_2\text{O}$ , is formed. L. Santi observed that cobalt carbonate is converted into the chloride when it is treated with an aq. soln. of ammonium carbonate, and ammonia and carbon dioxide are evolved; and by contact with solid ammonium chloride, or an aq. soln., the carbonate is converted into chloride. R. Salvadori noted that when cobalt dihydrazinechlorate is treated with carbon dioxide in the presence of an excess of hydrazine hydrate, **cobaltous trihydrazinecarbonate**,  $\text{CoCO}_3 \cdot 3\text{N}_2\text{H}_4$ , is formed. A. Naumann and J. Schröder, F. Schlegel, and A. Hantzsch observed that no change occurs when cobalt carbonate is heated with pyridine; N. A. Yajnik and F. C. Trehana, the photochemical reduction of sugars. C. Dufraisse and D. Nakae studied the catalytic effect on the oxidation of acetaldehyde, phenylaldehyde, purpuraldehyde, styrene, and turpentine. F. L. Cooper examined the absorption spectrum of soln. in acetic acid and sulphuric acid; A. Naumann and co-workers, that of cobalt carbonate dissolved in methyl acetate; S. U. Pickering, that it dissolves in tartaric, racemic, malic, and citric acids; L. I. Shaw, that the electrical conductivities of dimethyl sulphate, benzonitrole, aniline, amyl acetate, and salicylaldehyde are not altered by cobalt carbonate, but those of methyl alcohol, acetyl chloride, acetic anhydride, and epichlorhydrin are either increased or diminished; and I. I. Wanin and A. A. Tschernoyarova, that benzylidene chloride in an atm. of carbon dioxide at 60°, forms cobalt chloride and benzaldehyde. No definite product was obtained by P. N. Raikow in his study of the action of carbon dioxide on cobaltous hydroxide; but W. Beetz observed that hydrated cobaltous carbonate dissolves in water sat. with carbon dioxide, owing to the formation of an unstable **cobaltous hydrocarbonate**,  $\text{Co}(\text{HCO}_3)_2$ , when the aq. soln. is washed, cobaltous carbonate is deposited. G. Gore found that when 100 grms. of dry silica are added to 50 c.c. of a soln. containing 10 grms. of anhydrous cobalt carbonate, there is a rise of temp. of 0.21°.

As in the case of nickel carbonate, the salt is easily hydrolyzed by water, and a number of basic salts has been reported, several of which will be found to be arbitrarily selected stages in the hydrolysis of the salt.

W. Meigen treated a conc. soln. of cobalt nitrate with calcite and obtained **cobaltous hexahydroxycarbonate**,  $\text{CoCO}_3 \cdot 3\text{Co}(\text{OH})_2$ , or, according to A. Werner,  $[\text{Co}(\text{HO})_2\text{Co}]_3[\text{CO}_3]$ , as a blue precipitate; and by boiling a cobalt salt with an excess of sodium carbonate in an atm. of hydrogen for half an hour, he obtained the indigo-blue *monohydrate*. Sodium

carbonate is retained very tenaciously by the precipitate. Cobaltous salts in alkaline soln. are readily oxidized, so that W. Beetz reported that where the precipitate is boiled with water exposed to air, it becomes green, and develops chlorine when treated with hydrochloric acid. W. Meigen prepared **cobaltous tetrahydroxycarbonate**,  $\text{CoCO}_3 \cdot 2\text{Co}(\text{OH})_2$ , by treating a soln. of cobaltous nitrate with finely-powdered aragonite or calcite. With coarse fragments of calcite a mixture is produced. The product obtained with aragonite is said to resist attack by oxidizing agents better than the product with calcite. H. Rose described a *monohydrate* obtained by mixing boiling, dil. soln. of equimolar parts of cobalt sulphate and sodium carbonate, washing the violet precipitate with hot water, and drying it at  $100^\circ$ . W. Beetz treated a boiling soln. of a cobalt salt with the theoretical amount, or only a slight excess, of alkali carbonate, and obtained **cobaltous hexahydroxycarbonate**,  $2\text{CoCO}_3 \cdot 3\text{Co}(\text{OH})_2 \cdot \text{H}_2\text{O}$ , or, according to A. Werner,  $[\text{Co}(\text{HO})_2\text{Co}]_3(\text{CO}_3)_2\text{Co}$ , as a peach-blossom red precipitate, soluble in aq. soln. of ammonium, sodium, or potassium carbonate. If an excess of alkali carbonate is employed as precipitant, the precipitate is blue. W. Meigen observed that finely-divided aragonite gives, with a conc. soln. of cobalt nitrate, a lilac-coloured precipitate of this composition. The mol. of water is lost at  $95^\circ$ . If a soln. of cobalt chloride is used with aragonite or calcite, the precipitate has the same composition, but is contaminated with chlorine. W. Feitknecht said that the lattice has alternate layers of hydroxide and normal salt. Various kinds of precipitates obtained by G. C. Winkelblech, J. Setterberg, W. Beetz, W. Meigen, T. Nanty, C. D. Braun, F. Field, and H. Rose, had compositions ranging from  $\text{CoO}$ , 68.76 to 70.95;  $\text{CO}_2$ , 14.11 to 17.00; and  $\text{H}_2\text{O}$ , 12.03 to 14.94 per cent.—the theoretical values for  $2\text{CoCO}_3 \cdot 3\text{Co}(\text{OH})_2 \cdot \text{H}_2\text{O}$  are  $\text{CoO}$ , 70.05;  $\text{CO}_2$ , 16.51; and  $\text{H}_2\text{O}$ , 13.44 per cent. N. A. Jainik and F. C. Trehana studied the photosynthetic activity of cobalt carbonate in the reaction with carbon dioxide. W. Beetz reported **cobaltous dihydroxycarbonate**,  $\text{CoCO}_3 \cdot \text{Co}(\text{OH})_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ , by the action of sodium hydrocarbonate on a soln. of a cobalt salt, when the product is treated, with water, particularly warm water, it passes into the hexahydroxycarbonate. T. Nanty obtained the *tetrahydrate*,  $\text{CoCO}_3 \cdot \text{Co}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ . C. D. Braun also reported a lilac-red product approximating **cobaltous dihydroxycarbonate**,  $2\text{CoCO}_3 \cdot \text{Co}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$ , which loses the whole of its water of hydration at  $100^\circ$ , and at  $200^\circ$  forms hydrated cobaltous oxide.

J. J. Berzelius noted that these basic carbonates are soluble in carbonic acid, in soln. of alkali hydrocarbonates, and ammonium carbonate; slightly soluble in conc. soln. of sodium or potassium carbonate, and in aq. ammonia. R. H. Brett noted the solubility of the basic carbonate in cold soln. of ammonium nitrate or chloride. V. Lenher and C. H. Kao observed that the basic carbonate is very little attacked by selenium monochloride; and E. C. C. Baly and co-workers, that the basic carbonate absorbs carbon dioxide, and acts catalytically in the synthesis of carbohydrates from carbon dioxide and moisture. J. Spiller observed that the cobalt carbonates are not precipitated from soln. containing sodium citrate.

According to J. L. Proust, cobalt carbonate is soluble in aq. ammonia, or ammonium carbonate, and cobaltous hydroxide is soluble in a soln. of ammonium carbonate. The soln. are readily oxidized, and in air, a carmine-red liquid is produced which deposits crystals of cobalt carbonate. H. St. C. Deville obtained **ammonium cobaltous carbonate**,  $2(\text{NH}_4)_2\text{CO}_3 \cdot \text{CoCO}_3 \cdot 4\text{H}_2\text{O}$ , by adding ammonium carbonate to a soln. of cobalt nitrate, and allowing the mixture to stand. The red-currant coloured, prismatic crystals are stable in air at low temp. In addition to the *tetrahydrate*, the *enneahydrate*,  $2(\text{NH}_4)_2\text{CO}_3 \cdot \text{CoCO}_3 \cdot 9\text{H}_2\text{O}$ , and the *dodecahydrate*,  $2(\text{NH}_4)_2\text{CO}_3 \cdot \text{CoCO}_3 \cdot 12\text{H}_2\text{O}$ , were prepared. If ammonium hydrocarbonate, at  $15^\circ$  to  $18^\circ$ , be added to a soln. of cobalt nitrate, rose-red, micaceous crystals of **ammonium cobaltous hydrocarbonate**,  $\text{NH}_4(\text{HCO}_3) \cdot \text{CoCO}_3 \cdot 4\text{H}_2\text{O}$ , are formed, and in air, the crystals of the *tetrahydrate* lose ammonia and furnish a brown powder. By working at  $0^\circ$ , rose-red, micaceous plates of the *hemienneahydrate* are formed.

According to J. J. Berzelius, molten sodium carbonate dissolves a little cobalt oxide. When an excess of sodium carbonate is added to a soln. of a cobaltous salt, the red precipitate first formed dissolves so as to produce a red soln. According to H. St. C. Deville, if precipitated cobalt carbonate be allowed to stand under a soln. of sodium hydrocarbonate, the amorphous solid retains sodium very tenaciously, but no compound is formed. If a soln. of cobaltous nitrate be treated with the sodium hydrocarbonate,  $\text{Na}_2\text{CO}_3 \cdot 2\text{NaHCO}_3$ , carmine-red, monoclinic crystals

of **sodium cobaltous carbonate**,  $\text{Na}_2\text{CO}_3 \cdot \text{CoCO}_3 \cdot 4\text{H}_2\text{O}$ , are formed with the axial ratios  $a : b : c = 1.2295 : 1 : 1.0958$ , and  $\beta = 114^\circ 8'$ . M. P. Applebey and K. W. Lane obtained the tetrahydrate by heating at  $50^\circ$  a soln. of cobalt nitrate in a soln. of 100 grms. of sodium carbonate and 40 grms. of sodium hydrocarbonate per litre, and it can be re-crystallized from a soln. of these two sodium carbonates. F. de Carli obtained this carbonate mixed with a basic carbonate, by the action of a conc. of sodium carbonate on cobalt nitrate. The *tetrahydrate* is decomposed by water, and when heated, it loses water and carbon dioxide without melting. With more conc. soln., the *decahydrate*,  $\text{Na}_2\text{CO}_3 \cdot \text{CoCO}_3 \cdot 10\text{H}_2\text{O}$ , is formed. The colour is rather deeper than is that of the tetrahydrate. This salt loses some water in vacuo. C. Duval obtained **sodium cobalt percarbonate**, possibly  $\text{Na}[\text{CoCO}_4]$ , by the action of ozone on a mixed soln. of a cobaltous salt and sodium carbonate.

J. J. Berzelius observed that cobalt oxide dissolves freely in molten potassium carbonate; and J. L. Proust, that cobalt hydroxide and carbonate, but not the ignited oxide, form red soln. with a conc. soln. of potassium carbonate, and the solute is not precipitated by heat, but it is precipitated by dilution with water. H. St. C. Deville prepared quadratic prisms of **potassium cobaltous carbonate**,  $\text{K}_2\text{CO}_3 \cdot \text{CoCO}_3 \cdot 4\text{H}_2\text{O}$ , by adding the potassium hydrocarbonate,  $\text{K}_2\text{CO}_3 \cdot 2\text{KHCO}_3$ , to a soln. of cobalt nitrate; and W. C. Reynolds, by cooling a warm soln. of a cobalt salt and potassium carbonate.

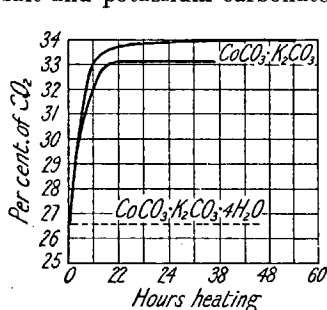


FIG. 141.—The Dissociation of Potassium Cobaltous Carbonate.

T. B. Wood and H. O. Jones obtained the tetrahydrate by adding potassium carbonate to a soln. of cobaltous chloride, and shaking the precipitate until it again dissolves; or making a soln. of 4 c.c. of a sat. soln. of cobalt chloride in 50 c.c. of a soln. of potassium carbonate (with 100 grms. of carbonate per 100 grms. of water). The soln. deposits crystals of the tetrahydrate. M. P. Applebey and K. W. Lane said that the salt exists only in presence of  $\text{HCO}_3^-$  ions, and treated a soln. of cobalt nitrate with a soln. of 400 grms. of potassium carbonate and 100 grms. of potassium hydrocarbonate per litre. The salt can be re-crystallized from a soln. of these two potassium carbonates.

The six-sided, rose-coloured prisms of the *tetrahydrate* are isomorphous with those of the corresponding nickel salt. F. de Carli studied the thermal dissociation of the carbonate, and found that the salt can be dehydrated at  $100^\circ$  to  $120^\circ$ , in a current of carbon dioxide, to furnish the deep violet, anhydrous salt. The dissociation press. is 63.42 mm. at  $220^\circ$ ; 389.80 mm. at  $280^\circ$ ; and 760 mm. at  $318^\circ$ , Fig. 141; and the heat of dissociation is 13.74 Cals., as in the case of the cobaltous carbonate. The heat of formation of the anhydrous carbonate from its elements is 460.17 Cals.,  $(\text{CoCO}_3, \text{K}_2\text{CO}_3) = 5.76$  Cals.; and  $\text{K}_2\text{CO}_3 \cdot \text{CoCO}_3 + 4\text{HCl} = 2\text{KCl} + \text{CoCl}_2 + 2\text{CO}_2 + 2\text{H}_2\text{O} + 17.75$  Cals. The heat of hydration to the tetrahydrate is 11.37 Cals. M. P. Applebey and K. W. Lane observed that at ordinary temp., the carbonate is stable; and it is decomposed by water; but T. B. Wood and H. O. Jones said that the aq. soln. is stable when heated, and that the colour changes from rose-red to blue. T. B. Wood and H. O. Jones said that the aq. soln. of the salt does not give any precipitate on boiling, but it becomes blue and returns to the original pink colour on cooling. From the behaviour of the soln. on electrolysis, it is probable that a pink complex  $\text{Co}(\text{CO}_3)_2^{--}$  ion is present. T. Nanty obtained a crystalline **potassium cobaltous hydrocarbonate**,  $\text{KHCO}_3 \cdot \text{CoCO}_3 \cdot 4\text{H}_2\text{O}$ ; cobaltous carbonate does not combine directly with potassium hydrocarbonate, and no equilibrium was observed in the action of water on the double carbonate. H. Rose, and H. St. C. Deville obtained this hydrocarbonate by adding an excess of potassium hydrocarbonate,  $\text{K}_2\text{CO}_3 \cdot 2\text{KHCO}_3$ , to a soln. of cobalt nitrate. The rose-red crystals effloresce in air, and are decomposed by water. T. Nanty said that the rose-red

crystals are isomorphous with those of the corresponding magnesium and nickel salts. When heated, the colour becomes violet as carbon dioxide and water are evolved. When heated in nitrogen, cobalt dioxide is formed; and water decomposes the salt.

G. A. Bilibin described a cobaltiferous smithsonite—**cobaltsmithsonite**—or **cobaltous zinc carbonate**,  $(\text{Co}, \text{Zn})\text{CO}_3$ , from Boles, Lower California. A. Ferrari and R. Santucci obtained **cobaltous cadmium carbonates**,  $\text{Co}_3\text{Cd}(\text{CO}_3)_4$ ,  $\text{CoCd}(\text{CO}_3)_2$ , and  $\text{CoCd}_3(\text{CO}_3)_4$ ; as well as corresponding **cobaltous manganous carbonates**.

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## § 26. Cobaltic Carbonate and its Complex Salts

W. Beetz<sup>1</sup> observed that a green cobaltic carbonate is produced by the oxidation of cobaltous carbonate. In 1862, F. Field observed that when cobaltous nitrate is added to a soln. of sodium hydrocarbonate containing a small proportion of sodium



hypochlorite, an intense green soln. is produced without the evolution of carbon dioxide. J. Gibson found that the same green colour is produced by bromine in the presence of sodium carbonate; N. C. Nag said that the green soln. so obtained gives a precipitate when shaken with alcohol and ether, and added that the precipitate is free from bromine, and it is very unstable. It was thought to be an oxidation product analogous to the ferrates. A. Job determined the atomic ratio of cobalt to oxygen in the green soln. to be  $\text{Co} : \text{O} = 2 : 3$  in agreement with the assumption that a cobaltic salt is present.

A. H. McConnell and E. S. Hanes showed that the green soln. contains alkali percobaltites, where cobalt dioxide takes the place of  $\text{MnO}_2$  in the permanganites. This conclusion is based on the observed atomic proportions  $\text{K} : \text{Co} = 2 : 1$ ; and because an acidic reaction was obtained with the colourless filtrate from a mixture of cobaltous hydroxide and hydrogen dioxide, the colourless soln. was assumed to contain *percobaltous acid*,  $\text{H}_2\text{CoO}_3$ . R. G. Durrant, however, observed no acidic reaction when purified hydrogen dioxide was employed. A. Metzl also found that in the moist state, the green precipitate obtained when hydrogen dioxide is added to a cobaltous salt in the presence of sodium hydrocarbonate, has the composition,  $\text{CoCoO}_3 \cdot \text{CoCO}_3$ , indicating that it is a mixture of *cobaltous cobaltite* and cobaltous carbonate. It is partly decomposed by washing with alcohol and ether.

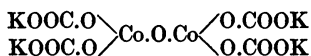
The preparation of the cobaltic carbonate by treating cobaltous salt soln. with oxidizing agents—hydrogen dioxide, chlorine or bromine, or alkali hypochlorite—was also described by A. H. McConnell and E. S. Hanes, A. Job, H. Copaux, and C. C. Palit. C. Duval used ozone as oxidizing agent; H. C. Byers electrolyzed a soln. of sodium hydrocarbonate with cobalt anodes; and G. A. Barbieri treated an alkali cobaltic nitrite with sodium hydrocarbonate—normal sodium carbonate produces hydrated cobaltic oxide—and the presence of  $\text{HCO}_3^-$  ions are, therefore, necessary for the production of cobaltic carbonate. E. Birk obtained the solid by the action of a soln. of sodium or ammonium carbonate on cobaltic fluoride,  $\text{Co}_2\text{F}_6 \cdot 7\text{H}_2\text{O}$ ; and C. Duval by the following process:

A conc., aq. soln. of 5 grms. of cobaltous carbonate was mixed, in the dark, with a conc. soln. of 8 grms. of sodium hydrocarbonate, 50 c.c. of 100 per cent. of hydrogen dioxide, and 100 grms. of an aq. soln. of glycerol of sp. gr. 1.262, with constant stirring in order to remove sodium carbonate. The olive-green powder has the composition  $\text{Co}_2(\text{CO}_3)_3$ , or  $\text{Co}[(\text{CO}_3)_2]$ , and it is filtered off, and washed with absolute alcohol. It is sensitive to light, and can be preserved in darkness.

R. G. Durrant obtained a green soln. on adding hydrogen dioxide to soln. of cobaltous salts in the presence of alkali hydrocarbonates, and suggested that a *cobaltic acid*,  $\text{H}_2\text{CoO}_4$ , is formed, because each atom of oxygen spent in oxidizing 2 atoms of cobalt, disengages two mols. of carbon dioxide. The observed results agree with the equation:  $4\text{KHCO}_3 + 2\text{CoCO}_3 + \text{H}_2\text{O}_2 = [\text{Co}(\text{KCO}_3)_2]_2\text{O} + 2\text{CO}_2 + 3\text{H}_2\text{O}$ . He also observed that green soln. and green precipitates were obtained by the use of various oxidizing agents in the presence of the hydrocarbonate, and concluded that the green soln. contained **cobaltic carbonate**,  $\text{Co}_2(\text{CO}_3)_3$ , and that the precipitate, which was fairly stable in an atm. of carbon dioxide, may be cobaltic carbonate itself.

N. C. Nag assumed that the cobalt is sexivalent; A. H. McConnell and E. S. Hanes, and A. Metzl, quadrivalent; and A. Job, R. G. Durrant, G. Barbieri, and R. Bernard and P. Job, trivalent, or a mixture of trivalent and quadrivalent. R. Bernard and P. Job, and R. G. Durrant studied the absorption spectrum of the soln.; and C. Duval, and G. A. Barbieri, the transport numbers. R. G. Durrant found that cobaltous oxide and salts form double salts with carboxylic acids—e.g., acetic, tartaric, citric, oxalic, lactic, malic, succinic, and glycollic acids—and on oxidation, green compounds are formed whose stability is increased by the presence of an excess of the alkali salt. The results indicate that a complex salt containing trivalent cobalt,  $:\text{Co.O.Co}:$ , is present, so that

in the case of the hydrocarbonate soln., the complex salt is probably **potassium cobaltic carbonate**,  $[\text{Co}(\text{KCO}_3)_2]_2\text{O}$ , or :



but no evidence of such a product was observed in the case of the normal carbonates. The green colour of these soln. is characteristic of cobaltic combinations with the carboxylic acids, and this, in turn, depends on the presence of complex ions containing the nucleus :  $\text{Co.O.Co} :$ . These conclusions are also in agreement with the absorption spectra of the soln.

O. W. Gibbs and F. A. Genth<sup>2</sup> prepared **cobaltic hexamminocarbonate**,  $[\text{Co}(\text{NH}_3)_6]_2(\text{CO}_3)_3 \cdot 7\text{H}_2\text{O}$ , by treating the corresponding chloride with the theoretical proportion of silver carbonate, and evaporating the yellow filtrate. The brownish-yellow, rhombic prisms of the *heptahydrate* may contain some acid carbonate, owing to the absorption of carbon dioxide from air. J. D. Dana said that the rhombic prisms have the axial ratios  $a : b : c = 0.6148 : 1 : 0.6460$ . F. M. Jäger regarded the salt as a *hexahydrate*. Observations were also made by A. Dubosc, and L. Jacobsen. When the salt is dried in air, O. W. Gibbs and F. A. Genth observed that some water is given off, and the crystals become opaque. The salt is readily dissolved by hot water. By passing carbon dioxide into a soln. of the carbonate, brownish-red or brownish-yellow, monoclinic prisms of **cobaltic hexamminohydrocarbonate**,  $[\text{Co}(\text{NH}_3)_6](\text{HCO}_3)\text{CO}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ , were formed. J. D. Dana, and F. M. Jäger gave for the axial ratios  $a : b : c = 1.131 : 1 : 0.819$ , and  $\beta = 71^\circ 44'$ . The salt does not lose its water of hydration in air, but it does so in vacuo; it is less soluble than the normal carbonate. L. Jacobsen obtained **cobaltic hexamminochlorocarbonate**,  $[\text{Co}(\text{NH}_3)_6](\text{CO}_3)\text{Cl}$ , from a mixture of sat. soln. of the chloride and carbonate, or by treating the chloride with potassium carbonate, and crystallizing from boiling water.

F. Claudet, and S. M. Jörgensen prepared **cobaltic aquopentamminocarbonate**, in aq. soln., by rubbing up the chloropentamminochloride, or bromopentamminobromide, with the theoretical proportion of silver carbonate, and a little water. It is also formed by the action of carbon dioxide on an aq. soln. of aquopentamminohydroxide. The red liquid has a strong alkaline reaction.

G. Vortmann and O. Blasberg described **cobaltic nitratopentamminocarbonate**, but A. Werner and N. Goslings showed that the product is really carbonatopentamminonitrate—*vide infra*. S. M. Jörgensen reported **cobaltic chloropentamminocarbonate**,  $[\text{Co}(\text{NH}_3)_5\text{Cl}](\text{CO}_3) \cdot 4\frac{1}{2}\text{H}_2\text{O}$ , to be formed by triturating the corresponding chloride with silver carbonate and a little water, and adding alcohol to the filtrate. The work must be done rapidly, or the aquopentammino-salt may be formed. The violet-red crystals of the *hemihydrate* are freely soluble in water, and the soln. has an alkaline reaction. The crystals lose nearly all their water of hydration on exposure to air; an aq. soln. of the weathered salt, on treatment with alcohol, gave dark violet prisms of a *hemihydrate*.

A. Werner reported **cobaltic hydrocarbonatopentamminobromide**,  $[\text{Co}(\text{NH}_3)_5(\text{HCO}_3)]\text{Br}_2$ , to be formed, as a violet-red powder consisting of fine needles, by passing carbon dioxide into a conc. soln. of hydroxy-bromide; and **cobaltic hydrocarbonatopentamminiodide**,  $[\text{Co}(\text{NH}_3)_5(\text{HCO}_3)]\text{I}_3$ , by passing carbon dioxide through an aq. soln. of the hydroxy-nitrate. The pale carmine-red, microscopic crystals are stable in air. They are sparingly soluble in water, and the soln. has an alkaline reaction. The cold, aq. soln. is stable, but when warmed, carbon dioxide escapes and the soln. reverts to the hydroxy-nitrate. Potassium iodide precipitates a polyiodide; and with 20 per cent. aq. ammonia, carbonatopentamminonitrate is formed. J. Kranig prepared **cobaltic carbonatopentamminochloride**,  $[\text{Co}(\text{NH}_3)_5(\text{CO}_3)]\text{Cl} \cdot \text{H}_2\text{O}$ ; and W. Kuhn and K. Bein studied the absorption spectrum. N. Goslings prepared **cobaltic carbonatopent-**

**aminobromide**,  $[\text{Co}(\text{NH}_3)_5\text{CO}_3]\text{Br}$ , and **cobaltic carbonatopentamminoiodide**,  $[\text{Co}(\text{NH}_3)_5\text{CO}_3]\text{I}$ .

G. Vortmann and O. Blasberg described a **cobaltic sulphatopentamminocarbonate**, but J. Kranig showed that the product is rather **cobaltic carbonatopentamminosulphate**,  $\{[\text{Co}(\text{NH}_3)_5]_2(\text{CO}_3)\}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ . It was obtained by the aerial oxidation of a cold soln. of cobaltous sulphate in aq. ammonia and ammonium carbonate. When alcohol is added to the soln., an oily liquid is precipitated, and this, with more alcohol, crystallizes. The crystals are unstable, and deliquesce in moist air. The air-dried *tetrahydrate* loses about  $1\frac{1}{2}\text{H}_2\text{O}$  over calcium chloride, and the remainder is lost at  $75^\circ$ , the salt decomposes at a higher temp. It is readily soluble in water.

G. Vortmann<sup>3</sup> obtained **cobaltic carbonatotetramminocarbonate**,  $[\text{Co}(\text{NH}_3)_4(\text{CO}_3)]_2\text{CO}_3 \cdot 3\text{H}_2\text{O}$ , from the mother-liquor left in the preparation of the hydrocarbonate; and S. M. Jörgensen, by triturating the iodide with freshly-precipitated silver carbonate and water, and precipitating from the filtrate with alcohol. The violet, rhombic plates of the *trihydrate* lose 3 mols. of water over sulphuric acid, and take them up again when exposed to moist air. The salt decomposes at  $100^\circ$ . The salt is readily soluble in water, and the soln. has an alkaline reaction; only one-third of the total carbonate is ionogenic. Sodium dithionate precipitates the salt almost completely from aq. soln. K. Tschibisoff and co-workers studied the reactions of this salt. When the aq. soln. is saturated with carbon dioxide, and alcohol is added, **cobaltic carbonatotetramminohydrocarbonate**,  $[\text{Co}(\text{NH}_3)_4(\text{CO}_3)]\text{HCO}_3 \cdot \text{H}_2\text{O}$ , is formed. G. Vortmann obtained this salt by oxidizing a conc. ammoniacal soln. of cobaltous carbonate, saturating the liquid with carbon dioxide, and precipitating the salt with alcohol. A. Miolati said that in attempting to prepare the corresponding thiocyanate by adding barium thiocyanate to a soln. of cobaltous sulphate, treating the filtrate with ammonia and ammonium carbonate, and passing a current of air through the liquid, he obtained a red precipitate of the carbonato-hydrocarbonate, since that salt is less soluble than the carbonato-thiocyanate. The red, prismatic crystals of the *monohydrate* were found by A. Miolati to decompose slowly at the temp. of the water-bath, losing more in weight than corresponds with the water of hydration. S. M. Jörgensen also noted that the salt decomposes at  $100^\circ$ ; and that when treated with hydrochloric acid, a cold, aq. soln. furnishes the diaquotetramminochloride, and a hot soln., the chloroaquotetramminochloride. A. Miolati found that the mol. electrical conductivities of soln. of a mol. of the salt in 32 and 1024 litres are, respectively, 59.45 and 79.18; and at infinite dilution, 82.6. It is hence inferred that hydrolysis does not occur, in aq. soln. that the soln. contains a salt of a dibasic acid with a univalent base, possibly **cobaltic carbonatotetramminopyrocarbonate**,  $[\text{Co}(\text{NH}_3)_4(\text{CO}_3)]_2(\text{CO}_2)_2\text{O}$ . G. Vortmann reported a basic salt, **cobaltic carbonatohydroxyaquotriamminohydroxide**,  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})(\text{CO}_3)]\text{OH} \cdot \frac{1}{2}\text{H}_2\text{O}$ , to be formed in preparing the carbonatotetramminocarbonate. It is precipitated by alcohol as an oil which, by repeated solution, and treatment with alcohol, ultimately crystallizes. R. Uehleke measured the magnetic rotation of the plane of polarization of light in soln. of the salt. A. B. Lamb and V. Yngve found that **cobaltic carbonatotetramminohydroxide** exists only in aq. soln. The mol. conductivities of soln. with 0.2683 and 33.32 mols per litre at  $0^\circ$ , are, respectively, 100.3 and 108.7—or, at the limit, 121.8—and the percentage ionization in these two soln. are, respectively, 85.3 and 89.2. J. Meyer prepared **cobaltic carbonatotetramminomethylsulphate**,  $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{CH}_3 \cdot \text{SO}_4$ .

A. Miolati reported the preparation of **cobaltic carbonatotetramminofluoride**,  $[\text{Co}(\text{NH}_3)_4(\text{CO}_3)]\text{F} \cdot 3\text{H}_2\text{O}$ . S. M. Jörgensen, and G. Vortmann and O. Blasberg prepared **cobaltic carbonatotetramminochloride**,  $[\text{Co}(\text{NH}_3)_4(\text{CO}_3)]\text{Cl}$ , by passing air, for 2 or 3 hrs., through a soln. of cobaltous chloride, and ammonium carbonate in conc. ammonia, and adding alcohol; also by adding alcohol to a soln. of the nitrate in conc. soln. of ammonium carbonate—*vide infra*, the nitrate; and by

tritulating freshly-precipitated silver chloride with the corresponding iodide. The rhombic plates first formed pass into four-sided and six-sided prisms when kept under the mother-liquor. The salt loses only a trace of water when confined over sulphuric acid; and it is decomposed at  $100^{\circ}$ . G. Vortmann and O. Blasberg supposed the salt to be a hemitrihydrate. E. Valla, Y. Shibata, and Y. Shibata and G. Urbain studied the absorption spectra of aq. soln. N. R. Dhar and G. Urbain measured the polarization tension—*vide supra*, the hexamminochloride. R. Schwarz and K. Tede noted that the soln. decomposes in ultra-violet rays. A. Werner found that alcoholic hydrogen chloride changes the salt into cis-dichlorotetramminochloride; and W. Schramm found that oxalic acid converts it into the oxalato-chloride, and warm malonic acid (below  $65^{\circ}$ ) forms malonato-chloride. The general reactions are like those of the nitrate. S. M. Jörgensen observed that sodium chloroaurate precipitates from a soln. of the corresponding nitrate, **gold cobaltic carbonatotetramminochloride**,  $[\text{Co}(\text{NH}_3)_4(\text{CO}_3)](\text{AuCl}_4) \cdot \frac{1}{2} \text{H}_2\text{O}$ , in brownish-red, rhomboidal plates or needles which are dehydrated at  $100^{\circ}$ . The salt is sparingly soluble in water; insoluble in alcohol.

S. M. Jörgensen prepared **cobaltic carbonatotetramminobromide**,  $[\text{Co}(\text{NH}_3)_4(\text{CO}_3)]\text{Br}$ , by a process analogous to that employed for the chloride. It loses no weight over sulphuric acid; and slowly decomposes at  $100^{\circ}$ . A. Uspensky and K. Tschibisoff studied the absorption spectrum; F. de Boer, the X-ray absorption spectrum; and A. Werner and A. Miolati, the mol. conductivity at  $25^{\circ}$ . E. Petersen found the mol. conductivities of soln. of a mol of the salt in 50, 2000, and 3200 litres of water were, respectively, 52.8, 59.2, and 70.7 at  $0^{\circ}$ , and 96.4, 104.3, and 131.3 at  $25^{\circ}$ . The subject was discussed by A. Werner and C. Herty, and by W. D. Harkins and co-workers. W. Schramm found that oxalic acid reacts forming the oxalato-bromide; and warm malonic acid, the malonato-bromide.

S. M. Jörgensen prepared **cobaltic carbonatohexamminiodide**,  $[\text{Co}(\text{NH}_3)_4(\text{CO}_3)]\text{I}$ , in brownish-violet needles, by a process analogous to that employed for the chloride. A. Uspensky and K. Tschibisoff studied the absorption spectrum. W. Schramm found that the salt is reduced to the cobaltous state by warm oxalic and malonic acids. F. Ephraim and P. Mosimann obtained **cobaltic carbonatotetrammino-triiodide**,  $[\text{Co}(\text{NH}_3)_4(\text{CO}_3)]\text{I}_3$ , as a black aggregate of crystals, by the action of a soln. of iodine and potassium iodide on the corresponding nitrate. The salt decomposes at  $140^{\circ}$ . They also prepared **mercuric cobaltic carbonatopentamminiodide**,  $2[\text{Co}(\text{NH}_3)_4(\text{CO}_3)]\text{I} \cdot \text{HgI}_2$ , as a bluish-red precipitate, by adding alcohol to a soln. of the corresponding nitrate and potassium chloromercurate; and **bismuth cobaltic carbonatotetramminiodide**,  $[\text{Co}(\text{NH}_3)_4(\text{CO}_3)]\text{I} \cdot \text{BiI}_3$ , as a reddish-yellow precipitate, by adding bismuth iodide to a soln. of the iodide.

G. Vortmann, R. Pers, and G. Vortmann and O. Blasberg prepared **cobaltic carbonatotetramminosulphate**,  $[\text{Co}(\text{NH}_3)_4(\text{CO}_3)]_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ ; and S. M. Jörgensen recommended adding a soln. of cobaltous carbonate (20 grms.) in dil. sulphuric acid to a soln. of ammonium carbonate (100 grms.) in 250 c.c. of conc., aq. ammonia, passing a current of air through the liquid for 2 or 3 hrs. and evaporating the soln. with the addition of ammonium carbonate from time to time—*vide infra*, the nitrate. A. Uspensky and K. Tschibisoff obtained it by passing carbon dioxide into an aq. soln. of diaquatetramminosulphate, in the presence of calcium carbonate. The garnet-red prisms of the *trihydrate* were found by F. M. Jäger to be rhombic bipyramids with the axial ratios  $a : b : c = 2.2212 : 1 : 1.8003$ , sp. gr. 1.807 at  $20^{\circ}$ ; mol. vol. 290.0; and topic axial ratios  $\chi : \psi : \omega = 9.2630 : 4.1702 : 7.5075$ . On the other hand, L. W. Strock found the crystals to be monoclinic hemihedral, with the axial ratios  $a : b : c = 1.1132 : 1 : 0.7030$ , and  $\beta = 98^{\circ} 39'$ . There are three prominent cleavages parallel to the (100)-, (010)-, and the (102)-faces. The first is perfect, the other two are good. The ruby-red crystals are strongly pleochroic—the colour parallel to (100) is purple-red; that parallel to (010) is brownish-red

with a purple tinge; and that parallel to (001) is brownish-red. The index of refraction for the  $670\cdot2\mu$  ray is  $1\cdot6221$ ; for the  $658\mu$  ray,  $1\cdot6240$ ; for the  $610\mu$  ray,  $1\cdot6284$ ; and for the  $589\mu$  ray,  $1\cdot6320$ ; for the  $670\cdot2\mu$  ray,  $\alpha=1\cdot5973$ ,  $\beta=1\cdot6210$ , and  $\gamma=1\cdot6221$ ; and for the  $589\mu$  ray,  $\alpha=1\cdot5949$ ,  $\beta=1\cdot6309$ , and  $\gamma=1\cdot6320$ . The X-radiograms correspond with a unit cell having  $a=11\cdot80$  A.,  $b=10\cdot60$  A., and  $c=7\cdot12$  A.; and  $\beta=98^\circ 39'$ , which accommodates 2 mols. of the salt of sp. gr.  $1\cdot8816$  at  $22^\circ$ .

A. Benrath and W. Kohlberg observed an abrupt change in the curve representing the vap. press. and the mol. proportion of water, corresponding with the trihydrate. A. Gordienko, and A. Uspensky and K. Tschibisoff studied the absorption spectra of aq. soln.; and F. de Boer, the X-ray absorption spectra. K. Matsuno found the mol. conductivities of soln. with a mol of the salt in 100, 400, and 1600 litres at  $25^\circ$ , were, respectively, 78·83, 92·13, and 106·2. R. Schwarz and K. Tede observed that aq. solution occurs with soln. in the ultra-violet rays. L. W. Strock and T. P. McCutcheon observed that 100 c.c. of sat. soln. at  $25^\circ$  contained 6·061 grms. of the carbonato-sulphate. W. von Behren and I. Traube studied the subject. S. M. Jørgensen, and K. J. Pedersen measured the rate of decomposition of the salt. F. Ephraim found that dil. sulphuric acid converts the salt into the diaquo-sulphate, with the evolution of carbon dioxide. K. Matsuno studied the flocculating action on the hydrosol of arsenic sulphide. W. Schramm found that oxalic acid converts it into the oxalato-sulphate; and malonic acid, into the malonato-sulphate. The general reactions are like those of the nitrate.

G. Vortmann and O. Blasberg, and S. M. Jørgensen prepared **cobaltic carbonato-tetramminonitrate**,  $[\text{Co}(\text{NH}_3)_4(\text{CO}_3)]\text{NO}_3\cdot\frac{1}{2}\text{H}_2\text{O}$ , by the method analogous to that employed for the chloride and sulphate. H. and W. Biltz recommended the following process:

A soln. of 100 grms. of ammonium carbonate in 500 c.c. of water in a litre flask is mixed with 250 c.c. of conc., aq. ammonia, and then with a soln. of 20 grms. of cobalt carbonate in as little conc. nitric acid as possible, and diluted to 100 c.c. A vigorous current of air is then drawn through the liquid for 3 hrs. The colour of the liquid changes from deep violet to blood-red. The soln. is concentrated to about 300 c.c. in a porcelain dish, 5 grms. of powdered ammonium carbonate are added every 15 minutes—making about 25 grms. in all. The filtered soln. is boiled down to about 200 c.c. with the continued addition, in small lots at a time, of about 10 grms. of ammonium carbonate. The crystals which separate from the cooling soln. are washed first with a little water, then with dil. alcohol, and finally with alcohol alone. An impure crop of crystals can be collected by concentrating the mother-liquor; extracting the product at room temp., with 15 times its weight of water, precipitating the salt from the filtered soln. by adding 2 or 3 vols. of alcohol, and treating the precipitate as before. Yield, 22 to 25 grms.

The carmine-red, rhombic plates of the hemihydrate, according to S. M. Jørgensen, lose their water of hydration at  $100^\circ$ , and they take up the water again on exposure to moist air. A. Benrath and K. Andreas considered the salt to be the *monohydrate*. A. Uspensky and K. Tschibisoff measured the absorption spectrum; and F. de Boer, the X-ray absorption spectrum. Measurements of the electrical conductivity of aq. soln. by A. Werner and A. Miolati, and N. R. Dhar show that the salt is not stable in aq. soln. at  $25^\circ$  to  $30^\circ$ . H. Freundlich and G. Ettisch studied the electrokinetic potential. S. Berkman and H. Zocher found the magnetic susceptibility to be  $0\cdot22\times 10^{-6}$  mass unit; and the magnetic properties were studied by W. Biltz, and G. Depold. S. M. Jørgensen observed that 100 grms. of water dissolve 6·67 grms. of the salt. A conc., aq. soln. is deep red, and it gives precipitates with sodium dithionate, chloroaurate, or chloroplatinate; and with potassium iodide, or chloroplatinite. K. Matsuno studied the flocculating action on arsenic sulphide. F. Ephraim observed that precipitates are formed with nitronaphthalene- $\beta$ -sulphonic acid, and with dinitro-6-chlorobenzene-5-sulphonic acid. W. Schramm noted that oxalic acid yields the oxalato-nitrate, and warm malonic acid, the malonatonic nitrate.

A. Werner prepared a soln. of **cobaltic carbonatobisethylenediaminehydroxide**,  $[\text{Co en}_2(\text{CO}_3)]\text{OH}$ , by treating a soln. of the corresponding bromide with freshly-precipitated

silver oxide; and although the salt could not be isolated, the soln. was found by A. Werner, J. C. Duff, and T. S. Price and S. A. Brazier to be useful for building up complexes with dibasic organic acid radicles in the inner complex.

A. Werner and J. Rapiport, H. Seibt, H. E. Watts, E. Schmidt, and W. Tupizina prepared **cobaltic carbonatobisethylenediaminechloride**,  $[\text{Co en}_2(\text{CO}_3)]\text{Cl} \cdot \text{H}_2\text{O}$ , by heating trans-dichlorobisethylenediaminechloride with the theoretical proportion of sodium carbonate in aq. soln. The deep red soln. deposits dark red crystals of the *monohydrate*. The salt loses the water of hydration at  $70^\circ$  to  $80^\circ$ . The anhydrous salt was also prepared by J. Meisenheimer and co-workers. The absorption spectra of aq. soln. were studied by J. Angerstein, Y. Shibata, and K. Matsuno. W. Schramm found that with oxalic acid, the oxalato-chloride, and with malonic acid, probably, malonato-chloride are formed. A. Werner and T. P. McCutcheon treated the optically active dichloro-chlorides in a similar manner, and obtained red, crystalline powders of the *dextro-salt* and the *levo-salt*. The sp. rotation of 0.2 per cent. aq. soln. were  $[\alpha] = \pm 350^\circ$ . The soln. at  $90^\circ$  becomes inactive; and the activity of the soln. which has been kept for 14 days at ordinary temp., is about half its original value. K. Tschibisoff and co-workers studied these salts. J. C. Dippel and F. M. Jäger prepared **cobaltic carbonatobisdiaminotetramminochloride**,  $[\text{Co ptn}_2\text{CO}_3]\text{Cl}$ , with  $\alpha\beta\delta$ - and  $\beta\beta\delta$ -diaminopentanes.

A. Werner and J. Bösshart prepared **cobaltic carbonatobisethylenediaminebromide**,  $[\text{Co en}_2(\text{CO}_3)]\text{Br}$ , by the action of carbon dioxide on an aq. alkaline ice-cold soln. of cis- or trans-hydroxyaquobisethylenediaminebromide; and by A. Werner and J. Rapiport, and P. Pfeiffer and O. Angern, by the action of potassium bromide on the corresponding chloride. The salt crystallizes from its aq. soln. partly as a hydrate in dark red, hexagonal prisms, and partly as a brownish-red, crystalline crust. The hydrated form loses its combined water in air. The absorption spectra of aq. soln. were studied by A. Gordienko, and J. Angerstein. J. C. Duff found the mol. conductivities of soln. with a mol of the salt in 32, 256, and 1024 litres of water, at  $25^\circ$ , to be, respectively, 90.46, 103.5, and 106.1. E. Schmidt, and A. Werner and J. Rapiport prepared **cobaltic carbonatobisethylenediamineiodide**,  $[\text{Co en}_2(\text{CO}_3)]\text{I}$ , by the action of potassium iodide on the corresponding chloride. The dark red, prismatic crystals are sparingly soluble in water, since 100 grms. of water at  $80^\circ$  dissolve 1.43 grms. of the iodide. J. Angerstein, and Y. Shibata studied the absorption spectra of aq. soln. A. Werner and J. Rapiport obtained the optically active *dextro-salt*, and *levo-salt*, in a similar way, by starting from the corresponding optically active chlorides. The sp. rotations of 0.2 per cent. aq. soln. were  $[\alpha] = \pm 250^\circ$ . G. and P. Spacu prepared **silver cobaltic carbonatobisethylenediamineiodide**,  $[\text{Co en}_2(\text{CO}_3)]\text{AgI}_2$ ; and **mercury cobaltic carbonatobisethylenediamineiodide**,  $[\text{Co en}_2\text{CO}_3]\text{HgI}_2$ .

A. Werner and J. Rapiport prepared **cobaltic carbonatobisethylenediaminesulphate**,  $[\text{Co en}_2(\text{CO}_3)]_2\text{SO}_4 \cdot 5\text{H}_2\text{O}$ , by the action of a soln. of silver sulphate on a cold, sat. soln. of the iodide. The black, prismatic crystals of the *pentahydrate* become anhydrous at  $100^\circ$ . Silver nitrate acting on the bromide of the series, furnishes **cobaltic carbonatobisethylenediaminenitrate**,  $[\text{Co en}_2(\text{CO}_3)]\text{NO}_3 \cdot \text{H}_2\text{O}$ ; and P. Pfeiffer and O. Angern obtained the same salt by the action of potassium carbonate on a soln. of the trans-dichloronitrate, on a water-bath, and subsequently cooling the red liquid on ice. The bluish-red needles are soluble in water. A. Werner and J. Rapiport found that 100 grms. of water dissolve 5 grms. of the salt at  $60^\circ$ . J. Angerstein, and Y. Shibata studied the absorption spectra of aq. soln. J. Kranig obtained **cobaltic carbonatodecamminosulphate**,  $[\text{Co}_2(\text{NH}_3)_{10}\text{CO}_3](\text{SO}_4) \cdot 4\text{H}_2\text{O}$ .

A. Werner prepared **cobaltic carbonatobis(trimethylenediamine)chloride**,  $[\text{Co}(\text{NH}_2\text{CH}_2)_3\text{NH}_2)_2(\text{CO}_3)]\text{Cl} \cdot \text{H}_2\text{O}$ , in red needles, by heating an aq. soln. of the corresponding dichloro-chloride with the calculated proportion of sodium carbonate in aq. soln., and subsequent precipitation with alcohol. Cone. hydrochloric acid, or an alcoholic soln. of hydrogen chloride restores the original dichloro-chloride. If trans-dichloroethylenediaminediamminochloride be heated with a soln. of potassium carbonate, **cobalt carbonatobisethylenediaminediamminochloride**,  $[\text{Co}(\text{NH}_3)_2\text{en}(\text{CO}_3)]\text{Cl}$ , is formed in garnet-red crystals, easily soluble in hot water.

G. Vortmann reported **cobaltic tricarbonatohexammine**,  $[\{\text{Co}(\text{NH}_3)_3\}_2(\text{CO}_3)_3] \cdot 3\text{H}_2\text{O}$ , to be formed as a by-product in the preparation of the carbonatotetramminocarbonate, in the most soluble part. Alcohol precipitates a violet-red oil, which can be dissolved in water; and the soln., on evaporation in air, furnishes the crystalline salt.

O. F. Wiede and K. A. Hofmann prepared **cobaltic sulphodithiocarbonatohexammine**,  $[\{\text{Co}(\text{NH}_3)_3\}_2(\text{CS}_3)_2]\text{S}$ , by passing nitric oxide through a mixture of freshly-prepared cobaltous hydroxide, aq. ammonia and carbon disulphide. The salt, which is mixed with an amorphous by-product, is purified by washing with alcohol. It crystallizes in black, lustrous rhombohedra, dissolves sparingly in water, yielding a yellowish-green soln., and is soluble in sodium hydroxide, with a

dark green coloration, at first without evolution of ammonia. It is decomposed by strong acids, with precipitation of sulphur, and, when heated, gives off carbon disulphide. By prolonged heating with sodium hydroxide, all the nitrogen is given off as ammonia. It can also be prepared by warming a mixture of cobalt hydroxide, ammonia, and carbon disulphide. K. A. Hofmann found that the ammonia molecules of the salt  $\text{C}_2\text{S}_7\text{Co}_2(\text{NH}_3)_6$ , are only removed with difficulty by acids. Fuming hydrochloric acid, at the ordinary temp., yields  $\text{Co}_2\text{C}_2\text{ClS}_{14}\text{O}_{10}\text{H}_{26}$  as a black, crystalline precipitate, and a blue soln. is left. Acetic acid (60 per cent.), after many days at the ordinary temp., yields  $(\text{CS}_3)_3\text{Co}_2\text{S}(\text{NH}_3)_2\cdot\text{C}_2\text{H}_4\text{O}_2\cdot 4\text{H}_2\text{O}$ , whereby hydrogen sulphide is liberated and much cobalt dissolved. This salt crystallizes in small, lustrous black scales. Acetic anhydride acts very slowly, and after 4 days, yields  $\text{C}_2\text{S}_3\text{Co}_2\cdot 5\text{NH}_3$ , as a black, lustrous, crystalline powder. The above results show that no ammonia is combined between the cobalt and sulphur, for, if this were the case, groups of the constitution  $\text{CoNH}_3\cdot\text{S}\cdot\text{NH}_3\text{Co}$ , or  $\text{Co}\cdot\text{NH}_3\cdot\text{S}\cdot\text{C}$ , would be formed, and the compound  $\text{C}_2\text{S}_7\text{Co}_2(\text{NH}_3)_6$  should give the reactions of hydrogen sulphide or thiocarbonic acid. S. M. Jørgensen discussed this subject. K. A. Hofmann also prepared **cobaltic disulphodithiocarbonatoaquopentammine**,  $\text{Co}_2(\text{NH}_3)_5(\text{H}_2\text{O})(\text{CS}_3)_2\text{S}_2$ , by the action of diazobenzene nitrate on the triammine salt, at  $0^\circ$ , after 24 hrs. It forms black, prismatic crystals, is slightly soluble in water, and gives an intense green coloration with a dil. soln. of sodium hydroxide. With a large mass of diazobenzene nitrate and more prolonged action, more ammonia is eliminated. K. A. Hofmann prepared **cobaltic hydrosulphatothiocarbonato-triammine**,  $[\text{Co}(\text{NH}_3)_3(\text{CS}_3)(\text{HS})]$ , by allowing diazobenzene nitrate to act on the hexammine, at ordinary temp., for 4 to 5 days, when black prisms resembling hornblende are formed, from which the hexammine can be reproduced by eliminating the HS-group. The salt dissolves in water, with an intense yellow coloration; and in a soln. of sodium hydroxide or aq. ammonia, to a greenish-yellow soln.; neither of these solns. gives a coloration with sodium nitroferrocyanide, or a deposit of silver sulphide on a piece of metallic silver. It therefore does not contain ammonia between the cobalt and sulphur.

C. Duval prepared a red **sodium cobaltic percarbonate**,  $\text{Na}(\text{CoCO}_4)$ , by treating a sat. soln. of 5 grms. of hexahydrated cobaltous chloride, and 8 grms. of sodium hydrocarbonate, with ozone.

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### § 27. Cobaltous Nitrates

Anhydrous **cobaltous nitrate**,  $\text{Co}(\text{NO}_3)_2$ , was prepared by A. Guntz and F. Martin<sup>1</sup> by the action of nitric anhydride, or of a soln. of nitric anhydride in nitric acid, on hydrated cobaltous nitrate; and they also obtained it by the action of finely-divided cobalt on a soln. of silver nitrate in liquid ammonia:  $\text{Co} + 2\text{AgNO}_3 = 2\text{Ag} + \text{Co}(\text{NO}_3)_2$ . H. Lescœur, and R. Funk could not prepare the anhydrous salt by dehydrating the hydrate, since decomposition simultaneously occurs. According to F. A. C. Gren, W. A. Lampadius, J. L. Proust, H. Lescœur, B. Franz, G. C. Clark and H. K. Buckner, and N. A. E. Millon, a soln. of cobalt nitrate can be obtained by dissolving the metal, or the oxide, hydroxide or carbonate in dil. nitric acid; and when the carmine-red soln. is evaporated, it furnishes red, deliquescent crystals of the **hexahydrate**,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . J. C. G. de Marignac recommended evaporating the aq. soln. in vacuo, or cooling a conc. soln. V. M. Peshkova described the preparation of the salt. R. Funk, and F. Mylius and R. Funk studied the percentage solubility, *S*, of the salt in water, and found that:

	-18°	-22°	-29°	-23.5°	-22°	-10°	18°	55°	70°	91°
<i>S</i>	32.8	36.4	38.7	40.4	41.5	43.7	49.7	61.7	65.2	77.2
	Ice		$\text{Co}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$			$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$		$\text{Co}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$		

The trihydrate melts at 91°. There is a metastable system at 56° when *S*=62.9, and the solid phase is the hexahydrate. The results are plotted in Fig. 142. A. Gorbow suggested that a **tetradecahydrate**,  $\text{Co}(\text{NO}_3)_2 \cdot 14\text{H}_2\text{O}$ , may exist, but there are no facts to support the inference. The region of stability of the **enneahydrate**,  $\text{Co}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ , is indicated in the diagram; as it melts, it passes into the hexa-



hydrate. E. Frémy said that the crystals from a nitric acid soln. of the salt, dried in vacuo, are the *pentahydrate*, but this hydrate does not appear as a solid phase in the system:  $\text{Co}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ ; R. Funk found that the hexahydrate acquires the composition of the *tetrahydrate*, by the loss of 2 mols. of water, when it is confined

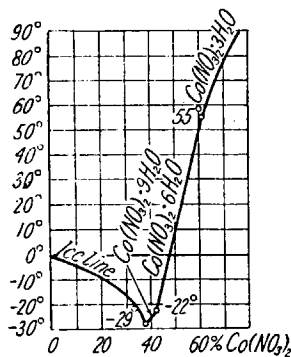


FIG. 142.—The Solubility of Cobalt Nitrate in Water.

over sulphuric acid for 8 days, but there is no evidence of the formation of this hydrate as a solid phase in the system:  $\text{Co}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ . The region of stability of the *trihydrate*,  $\text{Co}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , is also indicated in Fig. 142, and R. Funk obtained it by evaporating the molten hexahydrate between  $70^\circ$  and  $74^\circ$ . H. Lescœur obtained the trihydrate by adding an excess conc. nitric acid to a soln. of the hexahydrate. R. Funk said that decomposition occurs when the attempt is made to dehydrate the trihydrate, but J. G. Viana and E. Moles said that the *dihydrate* is formed, without decomposition, between  $60^\circ$  and  $70^\circ$ . G. L. Clark and H. K. Buckner obtained what they regarded as a dihydrate, by keeping the hexahydrate for 3 months over conc. sulphuric acid; and also by warming the molten hexahydrate between  $70^\circ$  and  $74^\circ$ . J. G. Viana and E. Moles said that when the hexahydrate is re-crystallized from fuming nitric acid it consists of a mixture of the dihydrate and trihydrate.

A. Guntz and F. Martin observed that the anhydrous nitrate is a pale pink powder; R. Funk said that the trihydrate appears in rhombic plates; and the hexahydrate, according to A. Ditte, is rose-red which becomes blue and then green as it loses water while in the molten state. K. Schaum and H. Wüstenfeld said that the hexahydrate is colourless at the temp. of liquid air. The hexahydrate was found by J. C. G. de Marignac to yield red, monoclinic crystals with the axial ratios  $a : b : c = 0.5875 : 1 : 0.9920$ , and  $\beta = 101^\circ 51'$ . The crystals were also described by C. F. Rammelsberg. A. V. Rakowsky and V. M. Peshkova studied the isomorphism of the magnesium and cobalt hexahydrates, and M. Hasselblatt, with nickel nitrate. H. Traube observed that the hexahydrate forms two series of solid soln. with zinc bromate, one of which is cubic, and the other monoclinic. J. W. Retgers observed no solid soln. is formed with ammonium nitrate. S. Jakubsohn and M. Rabinowitsch observed that when the hexahydrate is warmed in a glass vessel at  $21^\circ$  to  $22^\circ$ , the glass is usually broken by the dilation of the salt. C. H. D. Bödeker gave 1.83 for the **specific gravity** of the hexahydrate at  $14^\circ$ . B. Gossner gave 1.888; G. L. Clark and H. K. Buckner, 1.880 to 1.883; and J. G. Viana and E. Moles, 1.872 at  $25^\circ/4^\circ$ . G. L. Clark and H. K. Buckner gave 2.397 for the sp. gr. of the dihydrate. E. N. Gapon, and P. F. Gaehr studied the relation between the sp. gr. and the concentration of soln.; G. L. Clark and H. K. Buckner gave for the mol. vol. of the anhydrous salt, 73.5. The sp. gr. of aq. soln. of the salt was measured by A. Heydweiller, I. Traube, F. Dreyer, F. Fouqué, H. C. Jones and co-workers, B. Franz, and R. Funk. The *International Critical Tables* gave the following summary for soln. with  $C$  per cent. of anhydrous salt:

$C$	1	2	6	10	16	20	25	30 per cent.
Sp. gr. { $18^\circ$ .	1.0068	1.0317	1.0488	1.0848	1.1427	1.1841	1.2396	1.2998
{ $20^\circ$ .	1.0064	1.0145	1.0485	1.0840	1.1420	1.1840	1.2390	1.2990
{ $25^\circ$ .	1.0054	1.0135	1.0475	—	—	—	—	—

J. Wagner found for  $N$ -,  $0.5N$ -,  $0.25N$ -, and  $0.125N$ -soln., respectively, 1.0728, 1.0369, 1.0184, and 1.0094. B. Cabrera and co-workers gave for the effect of temp. on the sp. gr. of a soln. with 0.2435 gram.  $\text{Co}(\text{NO}_3)_2$  per litre,  $1.2515\{1 - 0.0043(\theta - 20)\}$ ; for one with 0.3679 gram. per litre,  $1.4254\{1 - 0.00047(\theta - 20)\}$ ; and for one with 0.4623 gram. per litre,  $1.5783\{1 - 0.00048(\theta - 20)\}$ . F. Dreyer observed that the

temp. of **maximum density** of soln. with 0.377, 0.767, 1.528, and 1.847 grms. per litre are, respectively, 3.40°, 2.79°, 1.64°, and 1.13°, when the value for water alone is 3.96°.

M. Torre studied the rate of **diffusion** of cobalt nitrate in aq. soln., and found that with soln. containing  $C$  grm.  $\text{Co}(\text{NO}_3)_2$  per 100 c.c., the rates of diffusion,  $R$ , represented by the difference in the amount of salt in 100 c.c at the beginning and end of 24 hrs., are :

	$C=0.915$			$C=0.366$			$C=0.185$		
	30°	40°	50°	30°	40°	50°	30°	40°	50°
$R$	0.229	0.353	0.475	0.094	0.147	0.188	0.053	0.070	0.098

G. Tammann studied the **inner pressure** of soln. Z. H. Skraup and co-workers measured the **capillary rise** of the soln. in bibulous paper. J. Wagner found the **viscosity**, of  $N$ -, 0.5 $N$ -, 0.25 $N$ -, 0.125 $N$ -soln. to be, respectively, 1.1657, 1.0754, 1.0318, and 1.0180 (water unity) at 25°. R. H. Adie found that for soln. with 0.05 and 0.025 mol  $\text{Co}(\text{NO}_3)_2$  per litre, the **osmotic pressures** are, respectively, 2.14 and 1.35 atm.; and the factor  $i$ , 1.35 and 2.42.

H. Lescœur said that the hexahydrate is fairly stable over sulphuric acid, although in moist air the crystals are very deliquescent; E. Frémy, however, said that the hexahydrate effloresces over conc. sulphuric acid, losing a mol. of water; R. Funk observed that 2 mols. of water are lost in 8 days, and that there is nothing to show that the product is a veritable *tetrahydrate*. H. Lescœur found that in the **thermal decomposition** of the hexahydrate water is given off when the hexahydrate is heated to 20°, and at 60° the vap. press. remains constant until 3 mols. have been withdrawn; after that, the vap. press. curve drops considerably. N. A. E. Millon observed that the crystals of the hexahydrate fuse below 100°, forming a violet-red liquid which gives off water, it then forms a green, viscid liquid which intumesces, with the evolution of nitrous fumes, to form black cobaltic oxide. W. A. Tilden reported that the **melting-point** of the hexahydrate is 38°, but this datum is too low; J. M. Ordway gave 56°, and this is in agreement with R. Funks' 55°; J. G. Viana and E. Moles gave 55.5° for the m.p. of the hexahydrate. The molten salt at this temp. is a supersaturated soln., and some trihydrate is formed as solid phase, which, at a higher temp., passes into soln. R. Funk added that the trihydrate melts at 91°, and any attempt to dehydrate this product by raising the temp. results in a simultaneous decomposition of the nitrate. A. Ditte, G. C. Winkelblech, and H. Lescœur noted the decomposition of the nitrate when the attempt is made to dehydrate the hexahydrate. R. Funk could not get beyond the trihydrate without decomposition; and G. L. Clark and H. K. Buckner, and J. G. Viana and E. Moles got as far as the dihydrate, and said that the dihydrate is fairly stable between 70° and 100°. A. Guntz and F. Martin found that the anhydrous nitrate begins to decompose between 100° and 105°, forming cobaltous oxide.

F. Fouqué measured the **thermal expansion**, or the change in vol.,  $\delta v$ , suffered by a soln. of  $C$  grms. of  $\text{Co}(\text{NO}_3)_2$  per 1000 grms. of water, as the temp. rises from 0° to  $\theta$ :

	$C=20$			$C=29.2$			$C=46.1$		
	12.1°	70°	92.5°	12.1°	70°	98.5°	11°	69.5°	99°
$\delta v$	0.00003	0.00029	0.00039	0.00008	0.00032	0.00040	0.00007	0.00034	0.00042

K. Jauch, and N. de Kolossowsky examined the **specific heat** of aq. soln. E. H. Riesenfeld and C. Milchsack gave 0.3733 cal. for the sp. ht. of the solid hexahydrate, and 0.5007 for the molten hexahydrate. H. Lescœur found that the **vapour pressure** of the hexahydrate is 100 mm. at 20°, and 58 mm. at 60°; that of the trihydrate is 30 mm. at 60°; and that of a saturated soln. of cobalt nitrate is about 9.3 mm. at 20°—*vide supra*. G. Tammann observed that the lowerings of the vap. press. of water at 100° by the dissolution of 15.38, 52.61, and 121.42

grms. of an anhydrous salt in 100 grms. of water are, respectively, 31.3, 144.3, and 358.4 mm. H. C. Jones and co-workers found the lowerings of the **freezing-point** of water,  $\delta\theta$ , by the dissolution of  $[\text{Co}(\text{NO}_3)_2]$  grms. of the anhydrous salt in 100 grms. of water to be :

$[\text{Co}(\text{NO}_3)_2]$ .	1.367	2.737	5.470	24.63	47.03
$\delta\theta$ .	0.352°	0.658°	1.388°	8.418°	26.500°

E. H. Riesenfeld and C. Milchsack calculated the latent **heat of fusion** to be 30.2 cal. J. Thomsen gave for the **heat of formation**  $(\text{Co}, \frac{1}{2}\text{O}_2, 2\text{HNO}_3\text{Aq.}) = 84.54$  Cals. ;  $(\text{Co}, \text{N}_2, 3\text{O}_2, 6\text{H}_2\text{O}) = 219.32$  Cals. ; and  $(\text{Co}, \text{O}_2, \text{N}_2\text{O}_4, 6\text{H}_2\text{O}) = 121.97$  to 123.33 Cals. ; whilst A. Guntz and F. Martin gave  $\{\text{Co}(\text{NO}_3)_2, 6\text{H}_2\text{O}_{\text{solid}}\} = 8.20$  Cals. ; and  $\{\text{Co}(\text{NO}_3)_2, 6\text{H}_2\text{O}_{\text{liquid}}\} = 16.84$  Cals. J. Thomsen gave for the **heat of neutralization**,  $(\frac{1}{2}\text{Co}(\text{OH})_2, \text{HNO}_3) = 10.546$  Cals. ; and for the **heat of solution** of a mol of the hexahydrate in 400 mols of water,  $-4.96$  Cals. A. Guntz and F. Martin gave for the heat of soln. of a mol of the anhydrous salt in 280 mols of water, 11.88 Cals. at 18°.

A. H. Pfund observed a maximum in the **reflected light** from the hexahydrate at  $7.45\mu$ . A. Bolland gave 1.52 for the **index of refraction** of the hexahydrate taken perpendicular to the direction of the edges of the prism. H. C. Jones and F. H. Getman gave for soln. with  $C$  mol of  $\text{Co}(\text{NO}_3)_2$  per litre, with the  $D$ -line :

$C$ .	0.0747	0.1495	0.2989	0.4484	0.7473	1.0462	1.4948
$\mu$ .	1.32700	1.32989	1.33395	1.33837	1.34606	1.35285	1.36347

and for soln. with 0.098 gm.  $\text{Co}(\text{NO}_3)_2$  per c.c., sp. gr. 1.078, with light of wave-length  $\lambda\mu$ , R. W. Roberts gave :

$\lambda$ .	589.3	420.0	400	380	360	350
$\mu$ .	1.3572	1.3620	1.3639	1.3663	1.3692	1.3705

Observations on the subject were also made by F. Fouqué, A. Hauke, A. Heydweiller, L. R. Ingersoll, and G. Limann. A. Hauke gave for the refraction of soln. with 3.12 and 1.41 per cent. of  $\text{Co}(\text{NO}_3)_2$ , with the  $C$ -line, and the  $\mu^2$ -formula, respectively (18.19) and 23.37. A. Heydweiller gave 23.07 for the  $D$ -line. A. Heydweiller also measured the dispersion. The **magnetic rotation** of the plane of polarized light,  $\omega$ , is negative, and R. W. Roberts gave for soln. with 0.098 gm.  $\text{Co}(\text{NO}_3)_2$  per c.c., sp. gr. 1.078, with a magnetic field of 13,510 gauss, at 20°, and light of wave-length  $\lambda\mu$  :

$\lambda$ .	589.3	420.0	400	380	360	350
$\omega$ .	0.0128	0.0242	0.0278	0.0317	0.0364	0.0394

M. Schérer and R. Cordonnier, P. K. Pillai, F. Allison and E. J. Murphy, E. Miescher, R. Wachsmuth, L. R. Ingersoll, and O. Schönrock also discussed the subject. M. Trautz observed no **crystalloluminescence** or **triboluminescence** of the hexahydrate.

M. Kimura and M. Takewaki made observations on the ultra-violet **absorption spectrum** of the hexahydrate. H. M. Vernon, J. H. Gladstone, and P. Vaillant discussed the effect of dilution and of the raising of the temp. on the colour of soln. of the nitrate—*vide supra*, the colour of cobalt chloride ; and the absorption spectrum of soln. of the nitrate was examined by F. L. Cooper, W. N. Hartley, R. Hill and O. R. Howell, R. A. Houstoun, H. C. Jones and co-workers, T. R. Merton, K. Schäfer, and P. Vaillant.

S. Jakobsohn and M. Rabinowitsch found the sp. **electrical conductivity**,  $K$  mhos, of the hexahydrate is :

	-10°	-1°	15°	23°	37°	42°	45.5°	46.5°
$K \times 10^5$ .	3.36	3.90	6.38	10.6	19.4	37.1	47.1	51.2

or  $\log K = -0.40052 + 0.014135\theta$  ; and for the molten salt :

	61.5°	67.0°	72.0°	77.0°	83.0°	87.0°
$K \times 10^2$ .	2.43	2.86	3.30	3.70	4.28	4.69

and they calculated that at 31°, the degree of loosening of the lattice is 0.0139.

The electrical conductivity of aq. soln. was measured by A. Heydweiller. E. Franke gave for the conductivity of a gram-equivalent of the salt in  $v$  litres at  $25^\circ$ :

$v$	32	64	128	256	512	1024
$\lambda$	93.63	98.56	102.2	105.8	108.7	111.2

H. C. Jones and J. N. Pearce found for the conductivity,  $\mu$ , of soln. with a mol of cobalt nitrate in  $v$  litres, and the calculated percentage **ionization**,  $\alpha$ :

$v$	100	40	20	10	2	1	0.5
$\mu$	108.66	100.69	96.12	89.94	72.94	58.89	37.10
$\alpha$	92.40	85.62	81.73	76.48	62.02	50.08	31.55

Observations were also made by W. H. Banks and co-workers, B. G. Whitmore, P. Vaillant, A. Heydweiller, H. C. Jones and F. H. Getman, H. C. Jones and A. P. West, and H. C. Jones and H. P. Bassett. L. Bruner found that the **hydrolysis** in aq. soln. of the nitrate is too small for measurement. C. Kullgren calculated for the degree of hydrolysis of soln. with an aq. of the salt in 8 and 32 litres, the respective values 0.00328 and 0.0152 per cent. at  $85.5^\circ$ , and 0.0048 and (0.0154) at  $100^\circ$ . H. C. Jones and co-workers calculated the **solvation** expressed as the number of mols. of water in combination with a mol. of the salt, if a litre of the soln., at that concentration, contained 1000 grms. of water. For soln. with  $C$  mols per litre:

$C$	0.0747	0.2989	0.7473	1.3451	2.0000	2.5700
Solvation	11.0	14.6	18.6	18.3	18.6	15.4

S. Labendzinsky measured the potential with soln. of cobalt nitrate—*vide supra*. L. F. Audrieth and L. F. Yntema studied the electrodeposition of cobalt from soln. of the nitrate in liquid ammonia; H. Brandes, the polarization of platinum in soln. of the nitrate; and A. Klemenc and H. F. Hohn, the glow electrolysis.

G. Jäger and S. Meyer found the **magnetic susceptibility** of soln. of cobalt nitrate to be  $56.8 \times 10^{-6}$  mass unit; and O. Liebknecht and A. P. Wills gave  $57.4 \times 10^{-6}$  mass unit. Observations were also made by G. Wiedemann, P. Plessner, A. Cabrera and co-workers, A. Heydweiller, P. Weiss and co-workers, H. Mosler, L. A. Welo, A. Trümpler, and P. Philipp. A. Quartaroli said that conc. soln. are paramagnetic; but with dil. soln., the diamagnetism of the water masks the paramagnetism of the salt. The neutral point occurs with soln. having 3.78 grms. of cobalt per litre. H. Stüdemann said that the susceptibility of the solid hexahydrate does not change when it is dissolved in water. A. Chatillon gave for the susceptibility of the soln.,  $\chi_{\text{soln}}$  mass unit, and of the dissolved  $\text{Co}(\text{NO}_3)_2$ ,  $\chi$  mass unit at different temp.:

	$11^\circ$	$19^\circ$	$49^\circ$	$81^\circ$	$105.5^\circ$	$128^\circ$
$\chi_{\text{soln.}} \times 10^6$	4.952	4.812	4.463	3.890	3.598	3.357
$\chi \times 10^6$	59.56	58.08	54.36	48.28	45.18	42.66

The effect of temp. was also measured by G. Wiedemann, G. Jäger and S. Meyer, and P. Plessner. B. Cabrera and co-workers gave for the sp. mol. susceptibility of soln.,  $\chi_{\text{mol}}$  mass unit, with  $C$  grm. of  $\text{Co}(\text{NO}_3)_2$  per gram of soln., at about  $25^\circ$ :

$C$	0.4623	0.05526	0.01737	0.00944	0.008056	0.005076
$\chi_{\text{mol.}} \times 10^6$	10,060	10,273	10,399	10,244	10,203	10,076

they also gave for the sp. susceptibility  $\chi_{\text{soln.}}$  mass unit, of the soln., with  $C$  per cent.  $\text{Co}(\text{NO}_3)_2$ , and of the  $\text{Co}(\text{NO}_3)_2$  mol.,  $\chi_{\text{mol.}}$  mass unit, at about  $25^\circ$ , in the presence of nitric acid—mol.  $\text{HNO}_3$  per mol.  $(\text{Co}(\text{NO}_3)_2)$ :

$C$	0.8056	0.8058	0.8062	0.8066	0.8075	0.8093
$\text{HNO}_3$	1.836	6.80	19.5	30.0	55.4	106.1
$\chi_{\text{soln.}} \times 10^6$	-0.5743	-0.5540	-0.5244	-0.4959	-0.4350	-0.3042
$\chi_{\text{mol.}} \times 10^6$	10,131	10,186	10,156	10,160	10,080	9990

Observations on the effect of concentration were made by P. Vaillant, P. Philipp, A. Heydweiller, and G. Falckenberg and R. Oppermann.

J. H. Weibel studied the action of **hydrogen**. J. L. Proust discussed the use of a soln. of cobaltous nitrate as a sympathetic ink (*q.v.*). V. N. Ipatéeff and B. Muromtzeff found that **hydrogen** at 200° to 300°, and 250 atm. press., precipitates cobaltic oxide from soln. of cobaltous nitrate; and S. Miyamoto, that the salt is reduced by hydrogen in the silent discharge. A. Mailfert studied the action of **ozone**. The hydrolysis and solubility of the salt in **water** have been already discussed. G. C. Winkelblech, and C. D. Braun found that the blue precipitate is obtained by adding an excess of ammonia to a well-boiled, aq. soln. of the nitrate. If air be not excluded, the precipitate turns grass-green, and gradually re-dissolves in the liquid, but a portion remains undissolved, and if this be washed with boiled water with the exclusion of air, and dried, it forms a grass-green powder which was considered to be **cobaltous decahydroxydinitrate**,  $\text{Co}(\text{NO}_3)_2 \cdot 5\text{Co}(\text{OH})_2$ . J. Habermann reported **cobaltous hexahydroxydinitrate**,  $\text{Co}(\text{NO}_3)_2 \cdot 3\text{Co}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$ , by dropping a very dil. soln. of ammonia into a well-stirred, boiling, conc. soln. of cobaltous nitrate. The colour is green on the outside, and blue in the interior. A. Bernadi observed the formation of a green precipitate with sodium hydroxide, as indicated in connection with the chloride (*q.v.*). W. Feitknecht said that the lattice corresponds with alternate layers of the normal salt and of the hydroxide. L. Archbutt, and H. Grossmann observed that a little cobalt nitrate favoured the decomposition of a soln. of **sodium dioxide**. D. Vitali found that **silver oxide** precipitates the hydroxide from aq. soln. of the nitrate.

K. Fredenhagen observed that cobalt nitrate is insoluble in liquid **hydrogen fluoride**. According to V. Cuvelier, a mixed soln. of cobaltous nitrate,  $\text{Co}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$ , and chloride,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , furnishes solid phases when it contains 40.68 per cent. of the nitrate, and 12.01 per cent. of the chloride. F. P. Venable observed that a conc. soln. of cobaltous nitrate mixed with **hydrochloric acid** is coloured green by ferric oxide. A. Schoep noted the occurrence in Katanga, Congo, of a hydrated **cobaltous chloronitrate**, in blue needles, presumably isomorphous with buttgenbachite,  $18\text{CuO} \cdot 0.3\text{Cl} \cdot \text{N}_2\text{O}_5 \cdot 19\text{H}_2\text{O}$ . The mineral was called **julienite**—after H. Julien. The refractive index of the tetragonal crystals is 1.556; and the sp. gr. is 1.594 at 20°. The crystals are soluble in water.

J. Thomsen found that the thermal value of the reaction of aq. soln. of cobaltous nitrate and **hydrogen sulphide**, is 3.68 Cals. E. Schürmann observed that a soln. of cobaltous nitrate is completely decomposed by **ferrous and manganous sulphides**, partially decomposed by **nickel sulphide**, and a little decomposed by **zinc sulphide**. C. Dufraisse and D. Nakae studied the catalytic action on the oxidation of soln. of **sodium sulphite**,

According to A. Ditte and F. Friedrichs, cobaltous nitrate is very sparingly soluble in **nitric acid**. A. Guntz and F. Martin noted that the anhydrous nitrate is soluble in liquid **ammonia**; H. Hunt and L. Boneyk said that the salt is insoluble in liquid ammonia at 25°; and E. G. Franklin and C. A. Kraus, that the hexahydrate forms a yellow soln. with liquid ammonia. The subject was studied by F. Friedrichs, and G. Yersin. H. Petzler studied the system:  $\text{Co}(\text{NO}_3)_2 \cdot \text{NH}_3 \cdot \text{H}_2\text{O}$ , at 25°. According to A. Guntz and F. Martin, if finely-divided cobalt reacts with silver nitrate dissolved in liquid ammonia, and the clear soln. evaporated, orange-red spangles of **cobaltous enneamminonitrate**,  $(\text{Co}(\text{NO}_3)_2 \cdot 9\text{NH}_3)$ , are formed. The salt explodes if heated rapidly, but if heated slowly, and exposed under reduced press., ammonia is given off, but before all the ammonia is expelled, nitrous fumes are evolved. The salt is decomposed by water, with the precipitation of cobaltous hydroxide. According to F. Ephraim and E. Rosenberg, G. L. Clark and H. K. Buckner, and G. L. Clark, **cobaltous hexamminonitrate**,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{NH}_3$ , is formed in rose-red, or reddish-brown crystals when trihydrated cobaltous nitrate is treated with dry ammonia. G. L. Clark and H. K. Buckner found the sp. gr. to be 1.473; E. Birk and W. Biltz gave 1.476 at 25°/4°; and W. Biltz found the

mol. vol. of the contained  $\text{NH}_3$ -groups is 22. F. Ephraim and E. Rosenberg gave for the dissociation press.,  $p$  mm.:

	21°	109.5°	131°	137.5°	152°	153°	157.5°	160°
$p$	13	129	209	271	471	535	650	(760)

L. J. Thénard, and E. Frémy reported a *dihydrate*,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{NH}_3 \cdot 2\text{H}_2\text{O}$ , to be formed when a conc., aq. soln. of cobaltous nitrate is treated with ammonia while air is excluded. The basic nitrate first precipitated dissolves in an excess of ammonia, forming a wine-red soln. which deposits rose-red crystals. These can be rapidly washed with aq. ammonia, pressed between bibulous paper, and dried in vacuo. The crystals were said to be stable in air, and to be decomposed by water, with the precipitation of a green basic salt. There is some doubt about the water of hydration. H. Hess found that the salt is soluble in ammonia.

H. Franzen and O. von Mayer obtained **cobaltous trihydrazinenitrate**,  $\text{Co}(\text{NO}_3)_2 \cdot 3\text{N}_2\text{H}_4$ , by heating a mixture of 10 grms. of cobaltous hexamminonitrate with 30 c.c. of 50 per cent. **hydrazine hydrate**, on a water-bath for 1 hr., washing the product with alcohol, and ether, and drying it in vacuo over conc. sulphuric acid and potassium hydroxide. The pale yellow powder explodes when heated, or when treated with conc. sulphuric acid. It is decomposed by hot water to form a green substance. S. Kitashima studied the oxidation of the soln. of cobaltous nitrate by **sodium bismuthate**.

J. H. Weibel studied the action of **carbon monoxide**. C. F. Wenzel observed that the hexahydrate is soluble in **ethyl alcohol**—the percentage solubility is about 7.4. P. Vaillant, F. L. Cooper, and R. A. Houstoun and co-workers discussed the absorption spectrum of the red soln. which is formed. H. A. Curtis and R. M. Burns obtained a wine-red soln. of the hexahydrate in **iso-amyl alcohol**—the soln. of the chloride is blue—the addition of hydrochloric acid turns the soln. blue; hydrogen sulphide precipitates nearly all the cobalt as sulphide—with the chloride only a small proportion is so precipitated; aq. ammonia gives a dirty green precipitate; and calcium bromide colours the soln. blue. F. W. O. de Coninck noted the solubility of the hexahydrate in **ethylene glycol**—100 grms. of a sat. soln. contain 80 grms. of  $\text{Co}(\text{NO}_3)_2$ . A. Grün and E. Boedecker obtained a complex salt with ethylene glycol, namely,  $\text{Co}(\text{NO}_3)_2 \cdot 3\text{C}_2\text{H}_4(\text{OH})_2$ ; with **propylene glycol**, a complex  $\text{Co}(\text{NO}_3)_2 \cdot 3\text{C}_3\text{H}_7(\text{OH})_2$ ; and with **pinacone**, the complex  $\text{Co}(\text{NO}_3)_2 \cdot 3\text{C}_6\text{H}_{12}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ . A. Naumann, and K. P. McElroy and W. H. Krug, noticed that it is readily soluble in **acetone**. The absorption spectrum of the red soln. was studied by R. A. Houstoun and co-workers; the electrical conductivity, by F. Bauer; and the magnetic susceptibility, by A. Quartaroli. A. Naumann observed that it is soluble in **methyl acetate**, and sparingly soluble in **ethyl acetate**. J. Schröder and H. Steiner said that 100 grms. of methyl acetate dissolve 16.4 grms. of  $\text{Co}(\text{NO}_3)_2$ ; and the raising of the b.p. of the red soln. shows that much ionization occurs. M. Stuckgold found the mol. conductivities of soln. of a mol. of the nitrate in 14.02, 32.81, and 91.54 litres of **urethane**, at 60°, are, respectively, 2.23, 2.36, and 2.80. T. Murayasu found the electrical conductivity of 0.5N- $\text{Co}(\text{NO}_3)_2$  is reduced by **glycine**. According to G. A. Barbieri and F. Calzolari, L. Vanino and A. Schinner, R. Rea, and G. Rossi, cobalt nitrate forms a complex with **hexamethylene-tetramine**; J. Reilly, and J. Reilly and W. J. Hickinbottom, one with *p*-**nitrosodi-n-butylaniline**; R. Cernatescu and co-workers, with **phenylenediamine**; J. Frejka and L. Zahlova, with **diaminobutane**; A. Naumann, G. Rossi, and F. Reitzenstein, one with **pyridine**; F. L. Hahn and co-workers, one with  $\alpha$ -**acetaminopyridine**; E. Borsbach, and F. Reitzenstein, one with **quinoline**; A. Rosenheim and V. J. Meyer, one with **thiocarbamide**; J. Moitessier, one with **phenylhydrazine**; and J. V. Dubsky and F. Brychta, one with **dimethylglyoxime**. E. J. Fischer obtained a bluish-violet precipitate with **imidazole**,  $(\text{C}_3\text{H}_4\text{N}_2)_3$ ; with **benzimidazole**,  $\text{C}_7\text{H}_6\text{N}_2$ , and with **3:5-dimethylpyrazole**; W. Hieber and E. Levy, with **mono-, di-, and trihydroxyethylamine**; and E. A. Jensen and E. R. Madsen, with

**thiosemicarbazide.** C. Dufraisse and D. Nakae studied the catalytic oxidation of **acetaldehyde**, **benzaldehyde**, **furfuraldehyde**, **styrene**, and **turpentine**.

T. Heymann and K. Jellinek studied the equilibrium of **nickel** in the soln,  $\text{Ni} + \text{Co}^{++} \rightleftharpoons \text{Co} + \text{Ni}^{++}$ . V. Cuvelier studied the ternary system **cobalt chloride**, **cobalt nitrate**, and **water**, at  $20^\circ$ ; no evidence of a complex was observed; and the only solid phases were  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , and  $\text{Co}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$ .

K. W. Wilcox and C. R. Bailey studied the ternary system:  $\text{Co}(\text{NO}_3)_2 - \text{Cu}(\text{NO}_3)_2 - \text{H}_2\text{O}$ , Fig. 143, and observed the formation of small, smoke-blue,

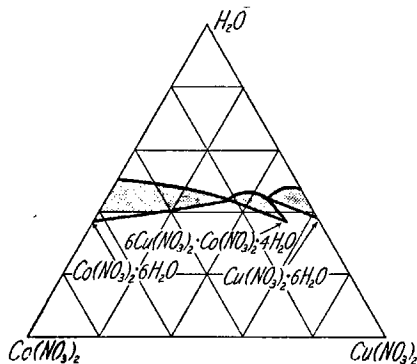


FIG. 143.—The Ternary System:  $\text{Cu}(\text{NO}_3)_2 - \text{Co}(\text{NO}_3)_2 - \text{H}_2\text{O}$ , at  $14^\circ$ .

deliquescent crystals of **copper cobaltous nitrate**,  $6\text{Cu}(\text{NO}_3)_2 \cdot \text{Co}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , at  $14^\circ$ , not at  $20^\circ$ ; the crystals melt at  $17^\circ$ , and are decomposed by water. W. Schrenzlowski discussed the isodimorphous solid soln. formed by copper and cobaltous nitrates. A. Mailhe reported **copper cobaltous trihydroxynitrate**,  $\text{Co}(\text{NO}_3)_2 \cdot 3\text{Cu}(\text{OH})_2$ , or, according to A. Werner,  $\text{Cu}_2(\text{OH})_4\text{Cu} = (\text{OH})_2\text{Co}(\text{NO}_3)_2$ , to be formed by the action of a soln. of cobaltous nitrate on  $4\text{CuO} \cdot \text{H}_2\text{O}$ . The green, monoclinic plates are isomorphous with those of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{CuO} \cdot 3\text{H}_2\text{O}$ . The salt was discussed by W. A. Endriss. F. T. Frerichs and E. F. Smith reported a *didymium cobaltous nitrate*,  $2\text{Di}(\text{NO}_3)_3 \cdot 3\text{Co}(\text{NO}_3)_2 \cdot$

$48\text{H}_2\text{O}$ , to be formed in dark red, deliquescent, and very soluble crystals from a soln. of the component salts. G. Jantsch likewise prepared **lanthanum cobaltous nitrate**,  $\text{Co}_3[\text{La}(\text{NO}_3)_6]_2 \cdot 24\text{H}_2\text{O}$ , of sp. gr. 2.131 at  $0^\circ/4^\circ$ , m.p.  $101.8^\circ$ , and 100 c.c. of a sat. soln. in nitric acid of sp. gr. 1.325, contain 10.92 grms. of hydrated salt at  $16^\circ$ ; and **cerous cobaltous nitrate**,  $\text{Co}_3[\text{Ce}(\text{NO}_3)_6]_2 \cdot 24\text{H}_2\text{O}$ , of sp. gr. 2.157 at  $0^\circ/4^\circ$ , m.p.  $98.5^\circ$ , and 100 c.c. of a sat. soln. in nitric acid of sp. gr. 1.325, contain 10.33 grms. of hydrated salt at  $16^\circ$ ; M. Holzmann, and R. J. Meyer and R. Jacoby prepared **eerie cobaltous nitrate**,  $\text{CoCe}(\text{NO}_3)_6 \cdot 8\text{H}_2\text{O}$ , in dark reddish-violet crystals from a soln. of the component salts in nitric acid; and R. J. Meyer and R. Jacoby obtained **thorium cobaltous nitrate**,  $\text{ThCo}(\text{NO}_3)_6 \cdot 8\text{H}_2\text{O}$ , in a similar manner. G. Jantsch prepared **praseodymium cobaltous nitrate**,  $\text{Co}_3[\text{Pr}(\text{NO}_3)_6]_2 \cdot 24\text{H}_2\text{O}$ , in wine-red crystals of sp. gr. 2.176 at  $0^\circ/4^\circ$ , m.p.  $97^\circ$ , and 100 c.c. of a sat. soln. in nitric acid of sp. gr. 1.325, contain 12.99 grms. of hydrated salt at  $16^\circ$ ; **neodymium cobaltous nitrate**,  $\text{Co}_3[\text{Nd}(\text{NO}_3)_6]_2 \cdot 24\text{H}_2\text{O}$ , in wine-red crystals of sp. gr. 2.195 at  $0^\circ/4^\circ$ , m.p.  $98.5^\circ$ , and 100 c.c. of a sat. soln. in nitric acid of sp. gr. 1.325, contain 15.16 grms. of hydrated salt at  $16^\circ$ ; **samarium cobaltous nitrate**,  $\text{Co}_3[\text{Sm}(\text{NO}_3)_6]_2 \cdot 24\text{H}_2\text{O}$ , in brownish-red crystals of sp. gr. 2.237 at  $0^\circ/4^\circ$ , m.p.  $83.2^\circ$ , and 100 c.c. of a sat. soln. in nitric acid of sp. gr. 1.325, contain 34.27 grms. of hydrated salt at  $16^\circ$ ; and **gadolinium cobaltous nitrate**,  $\text{Co}_3[\text{Gd}(\text{NO}_3)_6]_2 \cdot 24\text{H}_2\text{O}$ , in pale red crystals of sp. gr. 2.315 at  $0^\circ/4^\circ$ , m.p.  $63.2^\circ$ , and 100 c.c. of a sat. soln. in nitric acid of sp. gr. 1.325, contain 45.14 grms. of hydrated salt at  $16^\circ$ . G. Urbain and H. Lacombe obtained red crystals of **bismuth cobaltous nitrate**,  $3\text{Co}(\text{NO}_3)_2 \cdot 2\text{Bi}(\text{NO}_3)_3 \cdot 24\text{H}_2\text{O}$ , of sp. gr. 2.48 at  $16^\circ/16^\circ$ , and m.p.  $58^\circ$ . G. Jantsch observed that 100 c.c. of a sat. soln. in nitric acid of sp. gr. 1.325, contain 54.67 grms. of the hydrated salt at  $16^\circ$ . A. V. Rakowsky and V. M. Peshkova found that at  $14^\circ$  to  $17^\circ$ , hexahydrated **manganese cobalt nitrates** form a continuous series of solid soln.

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## § 28. Cobaltic Nitrate and its Complex Salts

G. C. Winkelblech<sup>1</sup> found that a soln. of cobaltous oxide in nitric acid forms some **cobaltic nitrate**,  $\text{Co}(\text{NO}_3)_3$ , but it is soon reduced to cobaltous nitrate by light and heat. H. Marshall obtained evidence of the formation of cobaltic nitrate in the electrolysis of a conc. soln. of cobaltous nitrate in a partitioned cell. The liquid became indigo-blue while the current was passing, but the original colour returned when the circuit was broken. The blue colour is supposed to be produced by the presence of unstable cobaltic nitrate. S. Kitashima oxidized a soln. of cobalt

nitrate in conc. nitric acid by sodium bismuthate, and observed that the blue filtrate contained cobaltic nitrate; if dil. nitric acid is employed, the soln. is red, but it shows the absorption spectrum of cobaltic nitrate. The degree of oxidation of a soln. with sodium bismuthate in the presence of a given proportion of nitric acid, attains a limit. The cobaltic nitrate soln. is gradually reduced when the soln. is kept for some time. The salt is known only in aq. soln., but a remarkable series of stable amino-salts have been prepared.

A. Rosenheim and I. Koppel observed that when nitrogen trioxide is passed into a slurry of cobalt carbonate, a brown soln. is formed which, on evaporation at room temp., furnishes black crystals of **cobaltosic oxynitritonitrate**,  $2\text{CoO} \cdot \text{Co}_2\text{O}_3 \cdot 3\text{N}_2\text{O}_3 \cdot \text{Co}(\text{NO}_3)_2 \cdot 14\text{H}_2\text{O}$ . It is not clear if the nitrate is an integral part of the compound, or simply an admixture. T. Suzuki also obtained analogous salts,  $\text{Co}_3''\text{Co}_2'''(\text{NO}_2)_6(\text{NO}_3)_2(\text{OH})_4 \cdot 12\text{H}_2\text{O}$ , and  $\text{Co}_4''\text{Co}_2'''(\text{NO}_2)_8(\text{NO}_3)_2(\text{OH})_4 \cdot 15\text{H}_2\text{O}$ .

### *The CoA<sub>6</sub> or Hexammine Family*

E. Frémy<sup>2</sup> prepared **cobaltic hexamminonitrate**,  $[\text{Co}(\text{NH}_3)_6](\text{NO}_3)_3$ , by the oxidation of an ammoniacal soln. of cobaltous nitrate in air; L. Jacobsen, by oxidizing an ammoniacal soln. of cobaltous nitrate, mixed with ammonium nitrate, by silver nitrate; J. B. Rogojsky, by the action of silver nitrate on a soln. of the corresponding chloride acidified with hydrochloric acid; O. W. Gibbs and F. A. Genth, by adding barium chloride to a soln. of the sulphate; and F. Rose, and S. M. Jörgensen, by treating an aq. soln. of the chloride with nitric acid. S. M. Jörgensen, and L. Jacobsen used iodine as oxidizing agent, and H. and W. Biltz thus describe this process:

Dissolve 24 grms. of cobalt carbonate by warming it with just enough nitric acid for dissolution, and dilute the filtered liquid to make 100 c.c. Add 200 c.c. of conc., aq. ammonia, and to the boiling liquid add, slowly at first, 25.4 grms. of iodine. The reaction is vigorous, and a pale yellowish-brown precipitate is formed. Iodine should all have been added in half an hour. After the mixture has stood 2 hrs.' cooling, filter and wash the precipitate with ammoniacal water. Boil the precipitate with 200 c.c. of approximately 56 per cent. nitric acid. The iodine is liberated, and can be partially recovered by placing two funnels to form a double cone in the neck of the flask. When all the iodine has been expelled, the precipitate is filtered off; drained by suction; washed first with water containing nitric acid, then with alcohol; and dried in the water-oven. Yield about 22 grms.

The crystals are yellow, or orange-yellow plates or needles, which J. D. Dana said belong to the tetragonal system, and have the axial ratio  $a : c = 1 : 1.016$ . The crystals were examined by F. M. Jäger. E. von Fedoroff discussed the isomorphism of the salt with the corresponding  $[\text{Ir}(\text{NH}_3)_6](\text{NO}_3)_3$ . E. Birk and W. Biltz gave 1.804 for the sp. gr. at  $25^\circ/4^\circ$ , and 192.5 for the mol. vol. E. Birk and W. Biltz also discussed the mol. vol. of the  $\text{NH}_3$ -groups. R. Robl observed no luminescence in ultra-violet light. A. Werner and A. Miolati found the mol. conductivity,  $\mu$ , of a soln. of a mol. of the salt in  $v$  litres of water, at  $25^\circ$ , to be:

$v$	.	.	128	256	512	1024	2048
$\mu$	.	.	329.7	355.1	380.8	397.0	413.4

P. Pascal gave  $-0.258 \times 10^{-6}$  mass unit for the magnetic susceptibility; W. Biltz, L. C. Jackson, R. Ladenburg, and E. Rosenbohm also studied the magnetic properties of the salt.

According to S. M. Jörgensen, 100 grms. of water dissolve 1.67 grms. of the salt, at ordinary temp., and it is almost insoluble in dil. acids. P. Mosimann, and F. Ephraim and P. Mosimann found that a sat., aq. soln. at  $18^\circ$  contains 1.974 grms. or 0.033 mol per litre; and J. N. Brönsted and A. Petersen, at  $0^\circ$ , 0.0202 mol, and at  $20^\circ$ , 0.052 mol per litre. J. N. Brönsted studied the action of some salts on the solubility. A. Benrath and H. Pitzler, and H. Pitzler studied the equilibrium conditions in the system:  $[\text{Co}(\text{NH}_3)_6](\text{NO}_3)_3 + 3\text{NH}_4\text{OH} \rightleftharpoons [\text{Co}(\text{NH}_3)_6](\text{OH})_3$ .

+3NH<sub>4</sub>NO<sub>3</sub>. E. Böhm oxidized an ammoniacal soln. of cobaltous nitrate in hydrofluoric acid, and washed the product with dil. hydrofluoric acid. Honey-yellow, tetrahedral crystals of **cobaltic hexamminofluonitrate**, [Co(NH<sub>3</sub>)<sub>6</sub>](NO<sub>3</sub>)<sub>2</sub>F, remained. S. M. Jörgensen warmed an ammoniacal soln. of cobaltous nitrate with a soln. of iodine and potassium iodide, and obtained small, rectangular prisms, which may be **cobaltic hexamminoiodonitrate**, [Co(NH<sub>3</sub>)<sub>6</sub>](NO<sub>3</sub>)<sub>2</sub>I, but more probably a solid of the nitrate and iodide. S. M. Jörgensen treated an ammoniacal soln. of the hexamminonitrate with dil. sulphuric acid, or sodium sulphate, and obtained orange-yellow octahedra of **cobaltic hexamminosulphatonitrate**, [Co(NH<sub>3</sub>)<sub>6</sub>](SO<sub>4</sub>)(NO<sub>3</sub>). A. Benrath, and A. Benrath and H. Würzburger observed that the solubilities of the salt, expressed in grms. of Co in 100 grms. of water in the presence of the following proportions of nitric acid—grms. per 100 c.c. of water—at 30°, were:

HNO <sub>3</sub>	.	.	0.000	1.107	2.922	4.600	6.380
Co	.	.	0.450	0.225	0.082	0.0521	0.0338

The curve remains continuous and the solid phase becomes pale in colour when the soln. contains 16 per cent. of HNO<sub>3</sub>. Below that concentration, the solid phase is [Co(NH<sub>3</sub>)<sub>6</sub>](NO<sub>3</sub>)<sub>3</sub>; and above that concentration, **cobaltic hexamminohydro-nitrate**, [Co(NH<sub>3</sub>)<sub>6</sub>](NO<sub>3</sub>)<sub>3</sub>.HNO<sub>3</sub>, which furnishes orange-yellow needles. F. W. Bergstrom observed no definite product is formed by a soln. of potassium amide in liquid ammonia. S. M. Jörgensen found that cold, sat., aq. soln. give precipitates with dil. nitric acid, and conc. hydrochloric or hydrobromic acid, potassium iodide, chromate, dichromate, ferrocyanide, ferricyanide, cobalticyanide, or chromicyanide, with sodium pyrophosphate, ammonium oxalate, and hydrochloroauric acid. Dil. sulphuric acid gives the sulphatonitrate; a mixture of hydrochloroplatinic acid and sulphuric acid gives a sulphatoplatinic salt; sodium hydrophosphate with ammonia gives a precipitate; and mercuric chloride gives no precipitate, but in the presence of hydrochloric acid, a double chloride is precipitated. E. Wilke-Dörfurt and co-workers studied **cobaltic hexamminodinitratofluosulphonate**, [Co(NH<sub>3</sub>)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>SO<sub>3</sub>F.

A. Werner and E. Berl obtained **cobaltic hexahydroxylaminenitrate**, [Co(NH<sub>2</sub>OH)<sub>6</sub>](NO<sub>3</sub>)<sub>3</sub>, in golden-yellow crystals, by treating the corresponding chloride with nitric acid, free from the lower oxides of nitrogen, and the product re-precipitated 3 or 4 times from a soln. in water. During the operations, the product is liable to explode, with the development of gas and the reduction of cobaltic to the cobaltous salt. C. S. Borzekowsky prepared the dextro- and lævo-forms of **cobaltic hydroxylaminebisethylenediamineamminonitrate**, [Co(NH<sub>3</sub>)(NH<sub>2</sub>OH)<sub>en</sub>]<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub>.

S. M. Jörgensen,<sup>3</sup> and L. L. Lehrfeld prepared **cobaltic trisethylenediaminenitrate**, [Co en<sub>3</sub>](NO<sub>3</sub>)<sub>3</sub>, by heating the hexamminonitrate, or the nitratopentamminonitrate, with an aq. soln. of monohydrated ethylenediamine; or by precipitation with alcohol from a soln. of the corresponding chloride in dil. nitric acid; and F. M. Jäger, by treating the corresponding bromide with a warm soln. of the theoretical proportion of silver nitrate, and evaporating for crystallization. The dark red, or brownish-red crystals were found by F. M. Jäger to be rhombic bipyramids with the axial ratios  $a : b : c = 0.8079 : 1 : 1.1279$ . The crystals were also studied by E. von Fedoroff. F. M. Jäger gave 1.694 for the sp. gr. at 17°, and 1.709 at 25°/4°; 250.94 for the mol. vol. at 17°; and for the topic axial ratios,  $\chi : \psi : \omega = 5.2476 : 6.5513 : 7.2983$ . J. Angerstein studied the absorption spectrum. A. Werner and C. Herty found the mol. conductivity,  $\mu$ , of soln. with a mol of the salt in  $v$  litres, at 25°,

$v$	.	.	125	250	500	1000	2000
$\mu$	.	.	294.69	316.40	363.63	359.84	375.19

E. Rosenbohm gave  $-0.300 \times 10^{-6}$  mass unit for the magnetic susceptibility, and L. C. Jackson studied the magnetic properties. S. M. Jörgensen observed that the salt is readily soluble in water; it is not precipitated from its aq. soln. by nitric acid; and when evaporated with hydrochloric acid, the nitrate passes into the chloride. A. Werner, and F. M. Jäger observed that by treating the active bromides with the theoretical pro-

portions of silver nitrate, the *dextro-salt* and the *lævo-salt* can be obtained in dark red crystals, which, according to F. M. Jäger, belong to the rhombic system, have the axial ratios  $a : b : c = 0.8652 : 1 : 0.6009$  for the *dextro-salt*, and  $0.8647 : 1 : 0.5983$  for the *lævo-salt*. No marked cleavage was observed. The sp. gr. of the *dextro-salt* is 1.725 at  $25^\circ/4^\circ$ , and of the *lævo-salt*, 1.729 at  $25^\circ/4^\circ$ . J. Angerstein studied the absorption spectrum. A. Werner found the sp. rotations of 1 per cent. soln. to be  $[\alpha] = 132^\circ$  for the *dextro-salt*, and  $-130^\circ$  for the *lævo-salt*. F. M. Jäger studied the mol. rotations of these salts. E. Rosenbohn found the magnetic susceptibility of the *dextro-salt* to be  $-0.341 \times 10^{-6}$  mass unit, and of the *lævo-salt*,  $-0.340 \times 10^{-6}$  mass unit. L. C. Jackson studied the magnetic properties of the salt.

P. Pfeiffer and T. Gassmann prepared soluble, yellow, acicular crystals of **cobaltic trispropylenediaminenitrate**,  $[\text{Co}(\text{pn}_3)](\text{NO}_3)_3$ , by adding the theoretical proportion of silver nitrate to the corresponding chloride; and E. Rosenbohn found the magnetic susceptibility of the *lævo-salt* to be  $-0.385 \times 10^{-6}$  mass unit. L. C. Jackson also studied the magnetic properties of the salt. F. M. Jäger and H. B. Blumendal obtained **cobaltic trans-triscyclopentanediaminenitrate**,  $[\text{Co}(\text{C}_5\text{H}_{12}\text{N}_2)_3](\text{NO}_3)_3$ , in red needles, by adding the theoretical proportion of silver nitrate to a soln. of the chloride. The *dextro-salt* and *lævo-salt* were obtained from the corresponding cyclopentanediamines. The *trihydrate* forms hexagonal crystals, and the *tetrahydrate* cubic crystals. The hydrates lose water on exposure to air. K. R. Lange, and A. Werner and C. Kreutzer prepared **cobaltic cis-bisethylenediaminediamminonitrate**,  $[\text{Co}(\text{NH}_2)_2\text{en}_2](\text{NO}_3)_3$ , along with the *trans-salt*, by the action of liquid ammonia on dinitratobisethylenediaminenitrate, and fractional crystallization from hot, neutral, aq. soln. The *trans-salt* is the less soluble form. If conc., aq. ammonia be used in place of liquid ammonia, or if the aq. soln. be not quite neutral, a syrupy liquid is produced instead of the dark reddish-yellow crystals. According to A. Werner and Y. Shibata, the optically active camphor bromosulphonates, or the active chlorides, in nitric acid soln., when treated with silver nitrate, yield the *dextro-salt* or the *lævo-salt* in golden-yellow crystals. The sp. rotations of 0.5 per cent. aq. soln. are  $[\alpha] = 46^\circ$  for the *dextro-salt*, and  $-44^\circ$  for the *lævo-salt*. R. von Arx, and J. Lifschitz studied the rotary dispersion. The corresponding **cobaltic trans-bisethylenediaminediamminonitrate** was obtained by A. Werner and co-workers, along with the *trans-nitratobisethylenediamine amminonitrate*, by the oxidation of *trans-isothiocyanatobisethylenediamineamminothiocyanate* with nitric acid—there is a smaller yield with the *cis-compound*; and by treating the corresponding chloride with nitric acid. The brown pyramids were found by F. M. Jäger to belong to the rhombic system, and to have the axial ratios  $a : b : c = 0.9473 : 1 : 0.6708$ . A. Werner and C. Herty found the mol. conductivity,  $\mu$ , of a soln. of a mol of the salt in  $v$  litres of water, at  $25^\circ$ , to be :

$v$	.	.	.	125	250	500	1000	2000
$\mu$	.	.	.	312.01	340.09	364.32	384.13	401.90

A. Werner and K. Dawe reported **cobaltic bispropylenediaminediamminonitrate**,  $[\text{Co}(\text{NH}_2)_2\text{pn}_2](\text{NO}_3)_3$ , to be formed, in thin, straw-yellow plates, where the corresponding chloride is evaporated twice with nitric acid (1:1). F. M. Jäger and H. B. Blumendal obtained **cobaltic trans-bisethylenediaminecyclopentanediaminenitrate**,  $[\text{Co}(\text{en}_2)(\text{C}_5\text{H}_{12}\text{N}_2)](\text{NO}_3)_3$ , in brownish-red needles, by treating the corresponding iodide with silver nitrate. F. M. Jäger reported **cobaltic bisethylenediaminephenanthroline nitrate**,  $[\text{Co}(\text{en}_2)(\text{C}_{12}\text{H}_8\text{N}_2)](\text{NO}_3)_3$ , by treating the iodide with silver nitrate. The crystals are triclinic with the axial ratios  $a : b : c = 0.9938 : 1 : 0.8574$ . W. A. Redeker prepared **cobaltic pyridinebisethylenediamineamminonitrate**,  $[\text{Co}(\text{NH}_2)_2\text{en}_2\text{py}](\text{NO}_3)_3$ . F. M. Jäger and P. Koets prepared **cobaltic bistriaminotriethylaminesexiesethylenediaminenitrate**,  $[\text{Co}_3\text{en}_6(\text{C}_6\text{H}_{18}\text{N}_4)_2](\text{NO}_3)_4\text{H}_2\text{O}$ , by treating the sulphate with barium nitrate. The reddish-brown crystals are monoclinic prisms with the axial ratios  $a : b : c = 1.2327 : 1 : 0.5582$ , and  $\beta = 64^\circ 34'$ . J. C. Dippel and F. M. Jäger prepared **cobaltic trisdiaminopentanenitrate**,  $[\text{Co}(\text{ptn}_3)](\text{NO}_3)_3$ , with  $\alpha\beta\delta$ - and  $\beta\beta\delta$ -diaminopentanes and J. C. Duff, **cobaltic succinatobisethylenediaminenitrate**.

O. W. Gibbs and F. A. Genth<sup>4</sup> prepared **cobaltic aquopentamminonitrate**,  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})](\text{NO}_3)_3$ , along with the hexammine nitrate, by the oxidation of ammoniacal soln. of cobaltous nitrate, followed by precipitation with nitric acid; O. W. Gibbs, and S. M. Jörgensen, by treating an ammoniacal, ice-cold soln. of the nitratopentamminonitrate with an excess of conc. nitric acid; A. Werner, by similarly treating the chloropentamminochloride; J. M. Krok, by the action of nitric acid on the corresponding iodosulphate; S. M. Jörgensen, by the action of nitric acid on the corresponding oxalate; and by J. C. Duff and E. J. Bills, by the action of nitric acid on the carbonatopentamminonitrate. The brick-red crystalline powder, monoclinic prisms or quadratic plates, was shown by J. D. Dana, and F. M. Jäger to have the axial ratios  $a : b : c = 0.7984 : 1 : 1.0338$ ,

and  $\beta=85^{\circ} 3'$ . S. M. Jörgensen observed that at about  $100^{\circ}$ , the solid loses a mol. of water to form cobaltic nitratopentamminonitrate, and the same change occurs very slowly—within a year—at ordinary temp. A. B. Lamb and J. W. Marden, observed that the vap. press. of the aquopentamminonitrate is about 4 mm. at  $25^{\circ}$ . A. B. Lamb and J. P. Simmons found the mol. heat of soln. in water to be  $-15.38$  Cals. at  $25^{\circ}$ . A. N. Nikolopoulos, and R. Luther and A. N. Nikolopoulos studied the absorption spectrum. A. Werner and A. Miolati measured the mol. conductivity at  $25^{\circ}$ ; and H. J. S. King observed the mol. conductivity,  $\mu$ , of a mol of the salt in  $v$  litres of water, at  $0^{\circ}$ , to be :

$v$ . . .	32	64	128	256	512	1024
$\mu$ . . .	163.0	179.0	197.6	212.2	225.9	238.0

The values at  $25^{\circ}$  were found by J. C. Duff to increase with time, and thus was attributed to the acceleration of the transformation of the aquo-nitrate into the nitrate-nitrate by contact with the platinum electrodes; the change is also favoured by the presence of sodium nitrate. S. M. Jörgensen found that 100 grms. of water, at  $15^{\circ}$ , dissolve about 5 grms. of the salt; N. S. Kurnakoff made observations on the subject; and F. Ephraim found that a sat., aq. soln., at  $17.5^{\circ}$ , contains 0.153 mol per litre; H. Pitzler, and A. Benrath and H. Pitzler studied the hydrolysis of the salt; and A. Benrath and H. Würzburger observed that in the presence of nitric acid the number of grams of cobalt in 100 grms. of water, at  $11^{\circ}$ , is as follows :

$\text{HNO}_3$ . . .	0.00	2.73	5.39	11.15	25.72 per cent.
Co . . .	0.785	0.298	0.132	0.087	0.067

The solubility thus decreases with increasing concentration of the nitric acid. The solid phase in contact with sat. soln. with concentrations up to 36 per cent.  $\text{HNO}_3$  is the aquopentamminonitrate; with between 36 and 48 per cent. nitric acid, the solid phase is **cobaltic aquopentamminohydrionitrate**,  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})](\text{NO}_3)_3 \cdot \text{HNO}_3$ ; and with over 48 per cent. of nitric acid, the nitrate-nitrate is formed, and the solid phase is  $[\text{Co}(\text{HN}_3)_5(\text{NO}_3)](\text{NO}_3)_2 \cdot \text{HNO}_3$ . S. M. Jörgensen prepared the aquopentamminohydrionitrate as a pale red solid, from a conc. nitric acid soln.; he found that at  $103^{\circ}$ , it loses a mol. each of water and nitric acid to form the nitrate-nitrate. F. Ephraim and W. Flügel treated a soln. of the corresponding iodide with 4 vols. of  $2N\text{-HNO}_3$ , and obtained octahedral crystals of what was thought to be either **cobaltic aquopentamminiodonitrate**,  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})](\text{NO}_3)_2\text{I}$ , or else an isomorphous mixture. S. M. Jörgensen, and F. Ephraim and W. Flügel also reported **cobaltic aquopentamminosulphatonitrate**,  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})](\text{SO}_4)\text{NO}_3$ , by crystallization of the nitrate from dil. sulphuric acid. The red, octahedral crystals lose no weight at  $100^{\circ}$ ; a sat., aq. soln., at  $19^{\circ}$ , contains 0.0486 mol per litre. A. Benrath observed that aq. ammonia converts the aquopentamminonitrate into the hexamminonitrate. According to S. M. Jörgensen, a conc., aq. soln. of the aquo-nitrate gives precipitates with potassium iodide, chromate, dichromate, chloroaurate, and ferrocyanide, with ammonium oxalate, hydrochloroplatinic and hydrobromoplatinic acids, sodium chloromercurate, pyrophosphate, and dil. sulphuric acid. No precipitate is formed with dil. hydrochloric or hydrobromic acid, mercuric chloride or sodium dithionate or hydrophosphate.

A. Werner prepared **cobaltic cis - aquobisethylenediamineamminonitrate**,  $[\text{Co}(\text{NH}_3)_2\text{en}_2(\text{H}_2\text{O})](\text{NO}_3)_3$ , by treating a sat., aq. soln. of the bromide with conc. nitric acid; the trans-salt separates out, leaving the cis-salt in soln. from which it is precipitated by the addition of alcohol and ether in the cold. The salt is freely soluble in water. The **cobaltic trans-aquobisethylenediamineamminonitrate** is formed, as just indicated, in red, prismatic crystals. M. Rosner prepared **cobaltic aquopyridinetetramminonitrate**,  $[\text{Co}(\text{NH}_3)_4\text{py}(\text{H}_2\text{O})](\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ .

G. Vortmann<sup>5</sup> prepared **cobaltic diaquotetramminonitrate**,  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2](\text{NO}_3)_3$ , by treating carbonatotetramminonitrate with cold, conc. nitric acid.

It was also prepared in this manner by S. M. Jörgensen, A. Benrath and K. Andreas, K. R. Lange, M. Rosner, and J. N. Brönsted and co-workers; F. Ephraim, by the action of conc. nitric acid on carbonatotetramminosulphate; and J. N. Brönsted and co-workers, by keeping the nitratoaquopentamminonitrate in aq. soln. According to F. Ephraim, the red, prismatic crystals *verpuffen* in the flame; and a sat., aq. soln., at 22°, contains 1.03 mol of the salt per litre. K. Andreas, and A. Benrath and K. Andreas found that the solubility diminishes down to a constant minimum value with increasing proportions of nitric acid in the soln. The diaquo-nitrate is not stable in contact with nitric acid, since it changes into the nitrato-nitrate,  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{NO}_3)](\text{NO}_3)_2$ . H. Pitzler, and A. Benrath and H. Pitzler studied the hydrolysis of the salt.

A. Werner and K. R. Lange prepared **cobaltic cis-diaquobisethylenediaminenitrate**,  $[\text{Co en}_2(\text{H}_2\text{O})_2](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ , by treating a cold, conc., aq. soln. of the bromide with conc. nitric acid, dissolving the product in water containing a little nitric acid, and precipitating the ice-cold soln. with alcohol. The red plates of the *monohydrate* lose their water over calcium chloride. They obtained **cobaltic trans-diaquobisethylenediaminenitrate**, by adding silver nitrate to a conc., aq. soln. of the corresponding bromide, at 25° to 30°, and cooling the soln.; or by treating an ice-cold conc., aq. soln. of the bromide with fuming nitric acid. The brownish-red needles crystallized from water acidulated with nitric acid, are not hydrated. A. Werner reported **cobaltic diaquobispyridinediamminonitrate**,  $[\text{Co}(\text{NH}_3)_2\text{py}_2(\text{H}_2\text{O})_2](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ , to be precipitated from an ice-cold, aq. soln. of the corresponding chloride, by means of conc. nitric acid, or ammonium nitrate. The red crystals are sparingly soluble in water, and the soln. has an acidic reaction. G. Lindenberg prepared **cobaltic diaquotrimethylenediaminenitrate**,  $[\text{Co tr}_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$ .

G. Vortmann prepared **cobaltic triaquotriamminonitrate**,  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_3](\text{NO}_3)_3$ , along with some other salts, by evaporating an ammoniacal soln. of cobaltous carbonate along with ammonium carbonate and then adding nitric acid for precipitation. S. M. Jörgensen obtained it, in deliquescent, carmine-red crystals, by evaporating an aged, aq. soln. of trinitratotriammine over sulphuric acid; and J. N. Brönsted and K. Volquartz, by adding the theoretical quantity of silver nitrate to dichloroaquotriamminochloride. The constitution was discussed by A. Werner, and A. Werner and A. Miolati. G. Bredig noted that the mol. conductivity,  $\mu$ , decreases as the  $\text{NH}_3$ -group is replaced by a  $\text{H}_2\text{O}$ -group, so that with soln. containing  $\frac{1}{2}$  mol of the salt in  $v$  litres of water:

$v$		125	250	500	1000	2000
$\mu$	Hexammine . . . . .	343.8	378.0	401.6	426.9	442.2
	Aquopentammine . . . . .	333.6	365.4	390.3	412.9	436.4
	Diaquotetrammine . . . . .	325.5	354.8	379.8	399.15	417.4
	Triaquotriammine . . . . .	317.7	339.0	361.1	383.8	392.6

J. N. Brönsted and K. Volquartz obtained **cobaltic tetraquodiamminonitrate**,  $[\text{Co}(\text{NH}_3)_2(\text{H}_2\text{O})_4](\text{NO}_3)_3$ , by adding a small excess over the theoretical proportion of silver nitrate to a soln. of green dichlorodiaquodiamminonitrate. The carmine-red soln. is unstable and gradually decomposes. The ionization constant,  $K$ , for the complex-ion  $[\text{Co}(\text{NH}_3)_2(\text{H}_2\text{O})_4]^{++}$ , approximates 0.00014 at 15°, and 0.00030 at 20°, and at infinite dilution, 0.00040 at 15°.

### *The CoA<sub>5</sub> or Pentammine Family*

E. Frémy<sup>6</sup> prepared **cobaltic nitratopentamminonitrate**,  $[\text{Co}(\text{NH}_3)_5(\text{NO}_3)](\text{NO}_3)_2$ , by heating an ammoniacal soln. of cobaltous nitrate which has been oxidized by air, with an excess of ammonium nitrate, or, according to O. W. Gibbs and F. A. Genth, with nitric acid. O. Künzel said that the product obtained by E. Frémy's process is a basic salt:  $2\text{Co}_2\text{O}_4 \cdot 5\text{N}_2\text{O}_5 \cdot 20\text{NH}_3$ . S. M. Jörgensen obtained it by heating aquopentamminonitrate, for many hours, at 100°, or, according to A. Benrath and K. Mienes, by heating it with conc. nitric acid, for many hours, on a water-bath. J. M. Krok and S. M. Jörgensen obtained this salt by oxidation with iodine in the following manner:

Twenty grms. of cobaltous carbonate are heated with the required amount of dil. nitric acid to convert it to nitrate, and 200 c.c. of conc., aq. ammonia are added. The boiling

soln. is then treated with a gram-atom of iodine for each gram-atom of cobalt, as indicated in connection with the preparation of the hexamminonitrate. After filtering off the hexamminonitrate from the cold soln., the filtrate is mixed with an excess of nitric acid, and heated 3 hrs. on the water-bath. When all the iodine has been expelled, the precipitate is filtered off; drained by suction, washed with water containing nitric acid, then with alcohol, and finally dried in a water-oven.

The red, octahedral crystals have a violet tinge, and, according to J. D. Dana, they are tetragonal bipyramids with the axial ratio  $a:c=1:0.6216$ . E. Birk gave 1.868 for the sp. gr. at  $25^{\circ}/4^{\circ}$ , and 176.7 for the mol. vol. A. B. Lamb and J. P. Simmons found the mol. heat of soln. in water, at  $25^{\circ}$ , to be 14.9 Cals. E. Valla, A. N. Nikolopoulos, and R. Luther and A. N. Nikolopoulos studied the absorption spectra of aq. soln. According to S. M. Jörgensen, 100 grms. of water at  $16^{\circ}$  dissolve 0.367 grm. of salt; and N. S. Kurnakoff, and J. N. Brönsted and co-workers studied the solubility of the salt in water, and in methanol. F. Ephraim observed that a sat. aq. soln. at  $18^{\circ}$  contains 0.0122 mol per litre. The nitratonitrate in aq. soln. is transformed into the aquo-nitrate. The process of aquation,  $[\text{Co}(\text{NH}_3)_5(\text{NO}_3)]^{+} \rightarrow [\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{+}$ , was found by A. B. Lamb and J. W. Marden to be a reaction of the first order, and at  $25^{\circ}$ , J. N. Brönsted calculated that in aq. soln. the velocity constant  $k=0.000361$  at  $15^{\circ}$ ;  $0.000757$  at  $20^{\circ}$ ; and  $0.00180$  at  $25^{\circ}$ . The aquation is independent of the initial concentration of the complex ion, and of the degree of acidity. On the other hand, A. B. Lamb and J. W. Marden observed that the reaction is retarded up to 25 per cent. in acidic soln. A. B. Lamb and J. P. Simmons calculated for the mol. heat of the aquation, 480 cal. at  $25^{\circ}$ . The reaction was also discussed by A. Benrath, and R. Luther and A. N. Nikolopoulos; and R. Schwarz and K. Tede found that the reaction is favoured by exposure to light. S. M. Jörgensen said that the salt is decomposed when heated with water. S. M. Jörgensen observed that hot, dil. aq. ammonia dissolves the nitratonitrate, forming the aquopentamminonitrate. According to A. Benrath, aq. ammonia at  $25^{\circ}$ , converts the nitratopentamminonitrate into hexamminonitrate at a rate which is proportional to the concentration of the ammonia. In consequence of the aquation of the salt, S. M. Jörgensen stated that some reactions in aq. soln. reported for the nitratonitrate, really apply to the aquo-nitrate. S. M. Jörgensen observed that with a freshly-prepared, cold, sat. soln. of the nitratonitrate, precipitates are obtained with potassium iodide, chromate, dichromate, and ferricyanide, with sodium dithionate, picrate, and chloromercurate, and with hydrochloroplatinic and hydrobromoplatinic acids; but not with dil. sulphuric acid, potassium chloraurate, hydrofluosilicic acid, sodium pyrophosphate, or ammonium oxalate.

S. M. Jörgensen prepared **cobaltic nitratopentamminochloride**,  $[\text{Co}(\text{NH}_3)_5(\text{NO}_3)]\text{Cl}_2$ , in reddish-violet octahedra, by shaking one of the corresponding salts of the series, say the nitrate, with dil. hydrochloric acid (1:1). F. Ephraim observed that a sat. aq. soln., at  $18^{\circ}$ , contains 0.0279 mol per litre. S. M. Jörgensen observed that warm water converts the nitratonitrate into the aquapentammine. The mol. conductivities of soln. with a mol of salt in 125, 500, and 200 litres of water, at  $25^{\circ}$ , were found by A. Werner and A. Miolati to be, respectively, 219.6, 247.6, and 285.2. There is also a marked increase in the conductivity with time—e.g., the mol. conductivity of a soln. of a mol of the salt in 250 litres changed from 250 to 290.2 in 24 hrs. This is taken to correspond with the aquation of the salt, a reaction studied by A. B. Lamb and J. W. Marden. J. N. Brönsted and co-workers studied the solubility in water, and in methanol. According to S. M. Jörgensen, if the salt be re-crystallized from hydrochloric acid, the chlorochloride is formed. The precipitate obtained by adding sodium chloromercuriate in the presence of sodium or ammonium chloride, is **mercuric cobaltic nitratopentamminotetrachloride**,  $[\text{Co}(\text{NH}_3)_5(\text{NO}_3)]\text{Cl}_2 \cdot \text{HgCl}_2$ . The scarlet-red prisms are decomposed by hydrochloric acid (1:1) into chloropentamminochloride and mercuric chloride. J. M. Krok described **mercuric cobaltic nitratopentamminechloride**,  $[\text{Co}_2(\text{NH}_3)_{10}(\text{NO}_3)_3](\text{HgCl}_3)_3$ .

S. M. Jörgensen prepared **cobaltic nitratopentamminobromide**,  $[\text{Co}(\text{NH}_3)_5(\text{NO}_3)]\text{Br}_2$ , in reddish-violet crystals, by a process analogous to that employed for the chloride. F. Ephraim found that a sat., aq. soln., at  $18^\circ$ , contains 0.0159 mol per litre; and A. Werner and A. Miolati found that the mol. conductivities of a soln. of a mol of the salt in 250, 500, and 2000 litres of water, at  $25^\circ$ , are, respectively, 270.9, 288.1, and 316.6; and that with a soln. with  $v=250$ , the mol. conductivity increases in 24 hrs. from 270.9 to 309.5. This corresponds with the aq. soln. of the salt. J. N. Brönsted and co-workers studied the solubility in water and in methanol. S. M. Jörgensen obtained reddish-violet crystals of **cobaltic nitratopentamminoiodide**,  $[\text{Co}(\text{NH}_3)_5(\text{NO}_3)]\text{I}_2$ , by adding potassium iodide to a soln. of the corresponding nitrate. F. Ephraim found that a sat., aq. soln., at  $18^\circ$ , contains 0.0271 mol per litre. J. N. Brönsted and co-workers studied the solubility in water and in methanol. S. M. Jörgensen prepared violet needles of **cobaltic nitratopentamminosulphate**,  $[\text{Co}(\text{NH}_3)_5(\text{NO}_3)]\text{SO}_4 \cdot \text{H}_2\text{O}$ , by adding alcohol to a soln. of the chloride in dil. sulphuric acid. Only a trace of water is lost from the monohydrate at  $100^\circ$ , but all is expelled at  $135^\circ$  to  $140^\circ$ . F. Ephraim found that a sat., aq. soln., at  $18^\circ$ , contains 0.0050 mol per litre.

A. Werner prepared **cobaltic cis-nitratobisethylenediamineamminonitrate**,  $[\text{Co}(\text{NH}_3)_2(\text{NO}_3)](\text{NO}_3)_2$ , by evaporating, on a water-bath, a mixture of conc. nitric acid and aquobisethylenediamineamminonitrate. The orange-yellow crystals are converted by conc. ammonia into bisethylenediaminediamminonitrate. The corresponding **cobaltic trans-nitratobisethylenediamineamminonitrate**,  $[\text{Co}(\text{NH}_3)_2(\text{NO}_3)](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ , is obtained by treating trans-aquo-nitrate with nitric acid. L. Cohn prepared **cobaltic nitratobisethylenediamineamminobromide**,  $[\text{Co}(\text{NH}_3)_2(\text{NO}_3)]\text{Br}_2$ .

J. N. Brönsted obtained **cobaltic nitratotetramminonitrate**,  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{NO}_3)](\text{NO}_3)_2$ , by warming 10 grms. of the carbonatotetramminonitrate with 50 c.c. of 10 per cent. nitric acid, adding 50 c.c. of conc. nitric acid to the clear soln. at  $100^\circ$ , cooling in ice for 15 mins., and washing the crystals with alcohol. The salt is purified by dissolving 10 grms. in 200 c.c. of 0.1N- $\text{HNO}_3$ , and adding 50 c.c. conc., nitric acid to the ice-cold liquid. The salt obtained by G. Vortmann and co-workers, and M. Rosner, by precipitation from an aq. soln. of the carbonato-nitrate with nitric acid, is considered by J. N. Brönsted to be the diaquotetramminonitrate. A. Werner and A. Miolati found the mol. conductivities of soln. of a mol. of the salt in 128, 512, and 2048 litres of water, at  $25^\circ$ , are, respectively, 306.1, 353.8, and 388.5. J. N. Brönsted, and J. N. Brönsted and R. Livingston found that the conductivity of the soln. increases with its age, corresponding with the transformation of the nitratotetramminonitrate into the diaquotetramminonitrate. The aquation:  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{NO}_3)]^+ + \text{H}_2\text{O} = [\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+} + \text{NO}_3^-$ , is dependent on the acidity of the soln., and the reaction is of the first order if the  $\text{H}^+$ -ion is not less than about 0.001N. The velocity constant,  $k$ , of the aquation in acidic soln. is  $0.0376 + 0.04107/[\text{H}^+]$  at  $15^\circ$ , and at  $20^\circ$ , it is  $0.03160 + 0.0432/[\text{H}^+]$ . H. Pitzler studied the equilibrium conditions in the system:  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{NO}_3)](\text{NO}_3)_2 - \text{NH}_3 - \text{H}_2\text{O}$ .

O. W. Gibbs and F. A. Genth<sup>7</sup> obtained what they regarded as a basic pentammino-salt, **cobaltic hydroxypentamminonitrate**,  $[\text{Co}(\text{NH}_3)_5(\text{OH})](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ , as a separation from a mixture of an aq. soln. containing nitratopentamminonitrate, ammonium nitrate, and aq. ammonia. A. Werner prepared it by warming aquopentamminonitrate with 5 times its weight of conc., aq. ammonia, and precipitating with alcohol; it can be re-crystallized by adding alcohol to the soln. in aq. ammonia. The violet-red scales of the *monohydrate* lose their water at  $80^\circ$ . The violet, aq. soln. has an alkaline reaction. It liberates ammonia from ammonium salts, to form aquopentammine-salts; with acetic anhydride it forms the acetatopentammine-salt; and with carbon dioxide, the hydrocarbonato-nitrate. H. J. S. King found the mol. conductivity of soln. with a mol of the salt in 128 and 1042 litres of water, at  $0^\circ$ , to be, respectively, 124.2 and 143.4; and of a mol of the salt in 32, 128, and 1024 litres of water, at  $25^\circ$ , respectively, 196.5, 229.5, and 266.2. E. Rosenbohm



gave  $-0.197 \times 10^{-6}$  mass unit for the magnetic susceptibility, and the magnetic properties were studied by W. Biltz, and L. C. Jackson.

A. Werner, and M. Rosner prepared **cobaltic hydroxyaquotetramminonitrate**,  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{OH})](\text{NO}_3)_2$ , as a reddish-violet mush of tabular crystals, by treating the corresponding bromide with sodium nitrate and filtering rapidly. The salt is very unstable in aq. soln., forming black hexol-dodecamminonitrate. H. J. S. King found the eq. conductivity, at  $0^\circ$ , to be :

$\nu$	.	.	.	32	64	128	256	512	1024	$\infty$
$\lambda$	.	.	.	99.8	109.9	117.5	123.2	128.1	131.8	141.7

M. Rosner prepared **cobaltic hydroxybispyridinetriamminonitrate**,  $[\text{Co}(\text{NH}_3)_3\text{py}_2(\text{OH})](\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$ .

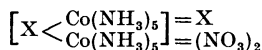
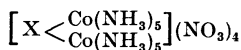
A. Werner prepared **cobaltic cis-hydroxyaquobisethylenediaminenitrate**,  $[\text{Co}(\text{en}_2)(\text{H}_2\text{O})(\text{OH})](\text{NO}_3)_2$ , by adding potash-lye to hexol-sexiesethylenediaminenitrate. Hydrated cobalt oxide first separates from the soln., and afterwards the required nitrate. M. Rosner prepared **cobaltic hydroxypyridinetriamminonitrate**,  $[\text{Co}(\text{NH}_3)_3\text{py}(\text{HO})](\text{NO}_3)_2$ . A. Werner obtained **cobaltic hydroxyaquobispyridinediamminonitrate**,  $[\text{Co}(\text{NH}_3)_2\text{py}_2(\text{H}_2\text{O})(\text{OH})](\text{NO}_3)_2$ , by adding a sat. aq. soln. of sodium nitrate to a soln. of the corresponding chloride in 10 per cent. acetic acid. The pale red needles have a bluish tinge; they are sparingly soluble in water, and the aq. soln. has a feebly alkaline reaction.

H. Seibt reported **cobaltic cis-fluobisethylenediamineamminonitrate**,  $[\text{Co}(\text{NH}_3)_2\text{en}_2\text{F}](\text{NO}_3)_2$ , to be formed as a red, crystalline powder, by treating the corresponding chloride with ammonium nitrate; and then adding alcohol to an aq. soln. of the salt.

A. Hiendlmayr<sup>8</sup> prepared **cobaltic fluopentamminonitrate**,  $[\text{Co}(\text{NH}_3)_5\text{F}](\text{NO}_3)_2$ , by adding dil. nitric acid to a sat. soln. of the corresponding fluoride or chloride. The violet-red powder is soluble in water, and in-hydrochloric acid.

S. M. Jörgensen, and R. Pers prepared **cobaltic chloropentamminonitrate**,  $[\text{Co}(\text{NH}_3)_5\text{Cl}](\text{NO}_3)_2$ , by adding conc. nitric acid to a soln. of the corresponding chloride or sulphate, and cooling to zero. Small, red, octahedral crystals are formed. S. M. Jörgensen observed no loss in weight occurs when the salt is heated to  $110^\circ$ , but there is a vigorous reaction at a higher temp. O. Stelling studied the X-ray absorption spectrum. A. Werner and A. Miolati found the mol. conductivities of soln. of a mol of the salt in 64, 256, and 2048 litres, at  $25^\circ$ , to be, respectively, 191.09, 212.8, and 232.6. A. B. Lamb and J. W. Marden found that the conductivity of the soln. changes with time, owing to aq. solution. The velocity constant of the aq. solution,  $k$ , corresponds with a reaction of the first order, and  $k=0.0455$ . R. Kremann studied the transport numbers; and L. C. Jackson, the magnetic properties. E. Rosenbohm gave  $-0.248 \times 10^{-6}$  mass unit for the magnetic susceptibility. J. W. Williams studied the activity coeff. S. M. Jörgensen said that the neutral, aq. soln. partially decomposes when boiled, but not so with the feebly acidic soln. J. N. Brønsted and co-workers studied the solubility of the salt in water, and in methanol. F. Ephraim and W. Flügel observed no precipitation with potassium nitrilosulphonate, but there is one with potassium hydroxylamine-iso-disulphonate.

J. C. Duff prepared pentamminonitrates with the dibasic radicles, X, of malonic, malic, phthalic, citraconic, itaconic, glutaric, and adipic acids of the types :



S. M. Jörgensen prepared **cobaltic cis-chlorobisethylenediamineamminonitrate**,  $[\text{Co}(\text{NH}_3)_2\text{en}_2\text{Cl}](\text{NO}_3)_2$ , by treating the corresponding chloride with dil. nitric acid, and then with alcohol. The pale carmine-red needles are readily soluble in water. The absorption spectrum was studied by A. Gordienko, and J. Angerstein. A. Werner and C. Hertý found that the mol. conductivities of soln. with a mol of the salt in 125, 500, and 2000 litres of water, at  $25^\circ$ , were, respectively, 204.90, 227.04, and 247.91. S. M. Jörgensen found that silver nitrate gives a precipitate only after the aq. soln. of the salt has been-boiled. A. Werner obtained **cobaltic trans-chlorobisethylenediamineamminonitrate**, by precipitating with alcohol a nitric acid soln. of the corresponding chloride. E. Berl prepared **cobaltic chlorobisethylenediaminehydroxylamine-nitrate**,  $[\text{Co}(\text{NH}_2\text{OH})\text{en}_2\text{Cl}](\text{NO}_3)_2$ . J. Meisenheimer

and E. Kiderlen obtained **cobaltic trans-chloroallylaminebisethylenediaminenitrate**,  $[\text{Co en}_2(\text{C}_3\text{H}_5\text{NH}_2\text{Cl})(\text{NO}_3)_2]$ , in six-sided prisms, by adding nitric acid to a soln. of the corresponding chloride. The crystals are dichroic—violet and green. They also prepared **cobaltic chloroanilinebisethylenediaminenitrate**,  $[\text{Co en}_2(\text{C}_6\text{H}_5\text{NH}_2\text{Cl})(\text{NO}_3)_2]$ , by adding an excess of sodium nitrate to a cold, aq. soln. of the corresponding chloride. The dark red crystals are easily soluble in water, and in conc. hydrochloric acid, but sparingly soluble in dil. nitric acid. They obtained **cobaltic chlorotoluidinebisethylenediaminechloronitrate**,  $[\text{Co en}_2(\text{C}_7\text{H}_7\text{NH}_2\text{Cl})(\text{NO}_3)\text{Cl}]$ , by the action of sodium nitrate on an aq. soln. of the corresponding chloride. The six-sided, violet-red prisms are feebly dichroic, and sparingly soluble in cold water. They prepared **cobaltic chlorobenzylaminebisethylenediaminenitrate**,  $[\text{Co en}_2(\text{C}_7\text{H}_7\text{NH}_2\text{Cl})(\text{NO}_3)_2]$ , by adding sodium nitrate to a soln. of the chloride. Rose-red plates are precipitated from the aq. soln. at  $50^\circ$  to  $60^\circ$ . R. Vogel obtained **cobaltic chloropyridinebisethylenediaminenitrate**,  $[\text{Co en}_2\text{pyCl}](\text{NO}_3)_2$ ; and C. Duval, **cobaltic tartaropentamminonitrate**,  $[\text{Co}(\text{NH}_3)_5(\text{C}_4\text{H}_4\text{O}_6)]\text{NO}_3$ .

S. M. Jørgensen<sup>9</sup> prepared **cobaltic cis-chloroaquotetramminonitrate**,  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{OCl})(\text{NO}_3)_2]$ , by triturating the corresponding chloride with cold water, acidulated with nitric acid, for complete soln., and precipitating the salt by nitric acid. The violet, rhombic crystals are decomposed at  $100^\circ$ —nitratopentamminochloride is one of the decomposition products. A. Werner, and A. Werner and A. Grün obtained **cobaltic chloroaquotriamminonitrate**,  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_2\text{Cl}](\text{NO}_3)_2$ , in bluish-violet needles, by adding nitric acid to a cold soln. of the corresponding chloride.

S. M. Jørgensen<sup>10</sup> prepared **cobaltic bromopentamminonitrate**,  $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{NO}_3)_2$ , by washing the corresponding bromide with water acidulated with sulphuric acid, at  $30^\circ$  to  $40^\circ$ , into cold, conc. nitric acid. The dark violet, octahedral crystals have a sp. gr. of 1.965 at  $17.1^\circ/4^\circ$ ; and I. Posen, and R. Lorenz and I. Posen gave 1.9632 for the sp. gr. in vacuo, and found the eq. conductivity of soln. with a gram-equivalent of the salt in 128, 512, and 1024 litres, at  $3.6^\circ$  to  $4.2^\circ$ , to be, respectively, 71.28, 76.89, and 78.29; and at  $18^\circ$ , 101.5, 108.6, and 109.5, when the eq. conductivity at infinite dilution is 116.4 at  $18^\circ$ . S. M. Jørgensen found the salt is soluble in water, and insoluble in dil. nitric acid, and in alcohol. J. N. Brønsted and A. Petersen found that a sat., aq. soln. contained 0.010 mol per litre at  $20^\circ$ ; and F. Ephraim, 0.0107 mol per litre at  $20^\circ$ . J. N. Brønsted and co-workers studied the solubility of the salt in water and in methanol. S. M. Jørgensen observed that silver nitrate precipitates no silver bromide from the freshly-prepared soln., but after standing for some time, or boiling for a short time, an opalescence appears, owing to the formation of silver bromide as the bromo-nitrate forms the aquo-nitrate. Hydrobromic and hydrochloric acids form the corresponding bromide or chloride. H. J. S. King prepared **cobaltic nitratoaquotetramminosulphate**,  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{NO}_3)]\text{SO}_4$ .

E. Schmidt, and A. Werner and W. E. Boës prepared **cobaltic cis-bromobisethylenediamineamminonitrate**,  $[\text{Co}(\text{NH}_3)_2\text{en}_2\text{Br}](\text{NO}_3)_2$ , by triturating the corresponding bromide with nitric acid, and re-crystallizing from its aq. soln. The dark reddish-violet, columnar crystals are almost black, and sparingly soluble in water. A. Werner and E. Scholze obtained the *dextro*-salt as a *monohydrate* from the corresponding camphorbromosulphonate. The dark violet crystals, in 0.08 per cent. aq. soln., have a sp. rotation  $[\alpha] = 45^\circ$  for red-light. If nitric acid be dropped into a cold, sat., aq. soln. of the bromide, **cobaltic cis-bromobisethylenediamineamminobromonitrate**,  $[\text{Co}(\text{NH}_3)_2\text{en}_2\text{Br}](\text{NO}_3)\text{Br}$ , is formed in reddish-violet crystals. A. Werner and W. E. Boës also prepared **cobaltic trans-bromobisethylenediamineamminonitrate**, as a *monohydrate*, by triturating lithium nitrate with the bromide and a little water. C. S. Borzekowsky prepared **cobaltic bromohydroxylaminebisethylenediaminenitrate**,  $[\text{Co}(\text{NH}_2)_2\text{en}_2(\text{NH}_2\text{OH})\text{Br}](\text{NO}_3)_2$ .

A. Werner and A. Wolberg<sup>11</sup> prepared **cobaltic cis-bromoaquotetramminonitrate**,  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Br}](\text{NO}_3)_2$ , by triturating the corresponding bromide, six times with dil. nitric acid (4 : 1), and washing the residue with alcohol and ether. The reddish-violet crystals are easily soluble in water. E. Schmidt, and A. Werner and E. Schmidt obtained **cobaltic cis-bromoaquobisethylenediaminenitrate**,  $[\text{Co en}_2(\text{H}_2\text{O})\text{Br}](\text{NO}_3)_2$ , as a bluish-violet crystalline powder, by adding sodium nitrate to a conc., aq. soln. of the corresponding bromide.

J. Sand and G. Bökman obtained **cobaltic iodopentamminonitrate**,  $[\text{Co}(\text{NH}_3)_5\text{I}](\text{NO}_3)_2$ , by triturating black nitrosopentamminonitrate with an alcoholic soln. of iodine, and boiling the green product with 20 per cent. nitric acid. A. Werner obtained the salt by mixing the nitro-nitrate with the iodo-nitrate, but preferably by triturating the corresponding dichromate or iodide with ammonium nitrate and a little water, and precipitating the salt from its aq. soln. by conc. nitric acid. J. Angerstein studied the absorption spectrum of aq. soln. The yellowish-green, crystalline powder is sparingly soluble in water—F. Ephraim added that a sat., aq. soln., at  $20^\circ$ , contains 0.00217 mol of the salt. A. Werner found that when warmed with silver nitrate in dil. acetic acid soln., the iodo-nitrate is converted into aquonitrate, with the precipitation of silver iodide.

S. M. Jörgensen<sup>12</sup> prepared **cobaltic sulphatotetramminonitrate**,  $[\text{Co}(\text{NH}_3)_4(\text{SO}_4)]\text{NO}_3$ , by treating an aq. soln. of the hydrosulphate with ammonium nitrate. The reddish-violet, four- or six-sided prisms lose no weight over sulphuric acid, or at  $100^\circ$ . F. Ephraim and W. Flügel observed that the sat., aq. soln. has 0.0273 mol of salt per litre at  $20^\circ$ ; and J. N. Brönsted and A. Peterson found 0.0260 mol per litre at the same temp. A. Werner and A. Miolati found the mol. conductivities of soln. with a mol of salt in 64, 256, and 1024 litres of water, at  $25^\circ$ , were, respectively, 78.63, 89.73, and 101.6. J. C. Duff added that the conductivity increases a little with time. P. Job found that when the soln. is titrated electrometrically with soln. of barium hydroxide, the curve is regular and shows no inflexion, and this is taken to indicate that no mols. of water are present in the radical. S. M. Jörgensen observed that with the aq. soln., barium chloride gives a precipitate of barium sulphate only after the soln. has been boiled; and dil. nitric acid, potassium iodide, and dichromate, and hydrochloroplatinic acid give crystalline precipitates of the corresponding salts.

F. Ephraim and W. Flügel prepared **cobaltic sulphatoaquotriamminonitrate**,  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})(\text{SO}_4)]\text{NO}_3$ , by adding ammonium nitrate to a conc., aq. soln. of the corresponding chloride. G. Vortmann and O. Blasberg also prepared this salt. The rose-red, prismatic crystals lose a mol of water slowly at  $100^\circ$ . F. Ephraim and W. Flügel found that a sat., aq. soln. has 0.0712 gram-atom of Co per litre at  $20^\circ$ . P. Job studied the electrometric titration of the salt with barium hydroxide. N. Goslings prepared **cobaltic carbonatotetramminonitrate**,  $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{NO}_3 \cdot \text{H}_2\text{O}$ ; and K. J. Pedersen studied the rate of decomposition of the salt.

#### *The $\text{CoA}_4$ or Tetrammine Family*

H. J. S. King<sup>13</sup> prepared **cobaltic dihydroxytetramminonitrate**,  $[\text{Co}\{\text{Co}(\text{NH}_3)_4(\text{OH})_2\}_3](\text{NO}_3)_6$ ; and E. Birk obtained **cobaltic dinitratotetramminonitrate**,  $[\text{Co}(\text{NH}_3)_4(\text{NO}_3)_2]\text{NO}_3 \cdot \text{H}_2\text{O}$ , by boiling and cooling a soln. of carbonatotetramminonitrate in nitric acid. The red crystals of the *monohydrate* lose their water at  $90^\circ$  to  $95^\circ$ . The sp. gr. of the monohydrate is 1.914 at  $25^\circ/4^\circ$ , and the mol. vol. 173.0; whilst the sp. gr. of the anhydrous salt is 1.939 at  $25^\circ/4^\circ$ , and the mol. vol. is 161.5. This salt resembles one prepared by G. Vortmann in 1885. W. Schramm obtained the salt by the action of malonic acid on the diaquotetramminonitrate, or on the hydroxyaquotetramminonitrate. Oxalic acid converts the salt into the oxalatonitrate; but malonic acid has no action. A. Werner and C. Kreutzer obtained **cobaltic dinitratobisethylenediaminehydronitrate**,  $[\text{Co en}_2(\text{NO}_3)_2]\text{NO}_3 \cdot \text{HNO}_3$ , in dark red, triclinic crystals, by evaporating to dryness a soln. of cis-dinitritobisethylenediaminenitrate with conc. nitric acid, dissolving the residue in conc. nitric acid, and evaporating over potassium hydroxide. When the hydronitrate is exposed to air, or confined over potassium hydroxide, it furnishes a greyish-brown powder of **cobaltic dinitratobisethylenediaminenitrate**,  $[\text{Co en}_2(\text{NO}_3)_2]\text{NO}_3$ , which is also prepared by evaporating the aq. soln. of the hydronitrate with conc. aq. ammonia, or by heating the hydrosulphate with liquid ammonia. The *monohydrate* was reported by W. Schramm to be formed by the action of malonic acid

on the diaquo-nitrate. The monohydrate decomposes slowly at  $120^{\circ}$ , and explosively above that temp.

H. Seibt<sup>14</sup> prepared **cobaltic cis-difluobisethylenediaminenitrate**,  $[\text{Co en}_2\text{F}_2]\text{NO}_3$ , in green plates, by evaporating trans-difluobisethylenediaminefluoride with water, mixing the cold, conc., aq. soln. with ammonium nitrate, and re-crystallizing the precipitate from water by the addition of alcohol. M. L. Ernsberger and W. R. Brode, and A. Gordienko studied the absorption spectrum.

A. Werner prepared **cobaltic cis-dichlorotetramminonitrate**,  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{NO}_3$ , by rubbing up the dithionate, with ammonium chloride, and then treating the cold, aq. soln. with nitric acid, and washing with alcohol and ether. The bluish-violet, six-sided plates are freely soluble in water and lose no weight over phosphorus pentoxide. A. Werner and A. Klein obtained **cobaltic trans-dichlorotetramminonitrate**, in green needles, by treating the hydrosulphate with conc. nitric acid. The salt was prepared by G. Vortmann and considered by him to be the monohydrate. O. Stelling studied the X-ray absorption spectrum. A. Werner and A. Miolati found that the mol. conductivity, at  $25^{\circ}$ , increases for a dilution of 512 litres per mol, from 133.5 to 323.0 in 1 hour, and the salt is completely transformed into the diaquo-nitrate. L. Tschugaeff made some observations on this subject. E. Rosenbohm found the magnetic susceptibility to be  $-0.175 \times 10^{-6}$  mass unit; and L. C. Jackson, and W. Biltz studied the magnetic properties. J. N. Brönsted and A. Petersen found that a sat., aq. soln., at  $0^{\circ}$ , contains 0.00383 mol per litre; they also studied the effect of the addition of other salts on the solubility of the dichloronitrate. A. Werner and A. Klein observed that silver nitrate gives a precipitate of silver chloride, after it has been warmed.

A. Werner and R. Feenstra prepared **cobaltic trans-dichloroquaterpyridinenitrate**,  $[\text{Co py}_4\text{Cl}_2]\text{NO}_3$ , by treating a soln. of the chloride with nitric acid; dissolving in water at  $40^{\circ}$  to  $50^{\circ}$ , and precipitating with conc. nitric acid; and re-crystallizing from dil. acetic acid. The green needles of the monohydrate lose their water of hydration over phosphorus pentoxide. T. S. Price obtained an air-dried salt with 4 to 5 mols. of water of hydration. The salt loses pyridine in a drying-oven. S. M. Jörgensen obtained violet prisms of **cobaltic cis-dichlorobisethylenediaminenitrate**,  $[\text{Co en}_2\text{Cl}_2]\text{NO}_3$ , by the action of dil. nitric acid on the corresponding chloride. O. Stelling studied the X-radiograms. The mol. conductivity of an aq. soln. with 150 litres per mol, was found by A. Werner and C. Herty to suffer very little change at  $0^{\circ}$  with time, but at  $25^{\circ}$  the conductivity changed from 97.38 to 123.45 in 19 mins., in consequence of the ionization of chlorine-ions liberated during the aq. solution of the complex salt. The subject was discussed by L. Tschugaeff, W. D. Harkins and co-workers, and E. Petersen. E. Rosenbohm found the magnetic susceptibility to be  $-0.287 \times 10^{-6}$  mass unit; and the magnetic properties were also studied by L. C. Jackson. P. Larisch, and A. Werner and P. Larisch found that 100 c.c. of water, at  $7^{\circ}$ , dissolve 0.566 gm. of the salt. S. M. Jörgensen observed that the salt is less soluble than the corresponding chloride, and that silver nitrate gives no precipitate with the cold soln., but a precipitate of silver chloride is produced if the soln. has stood for some time, or if it has been boiled. Hydrochloroplatinic acid gives a precipitate of chloroplatinate. A. Werner and G. Tschernoff obtained the *dextro*-salt and the *levo*-salt, in violet crystals, from the corresponding camphorbromosulphonates and nitric acid. A 0.25 per cent. soln. of the salt has the sp. rotations  $[\alpha] = \pm 164^{\circ}$ . S. M. Jörgensen prepared **cobaltic trans-dichlorobisethylenediaminenitrate**,  $[\text{Co en}_2\text{Cl}_2]\text{NO}_3$ , by adding nitric acid to an aq. soln. of the corresponding chloride. The emerald-green crystals do not dissolve in water so readily as the chloride; according to P. Larisch, and A. Werner and P. Larisch, 100 c.c. of water, at  $7^{\circ}$ , dissolve 0.346 gm. of the salt. O. Stelling studied the X-radiograms. A. Werner and C. Herty found that the mol. conductivity of a soln. with 125 litres per mol, at  $0^{\circ}$ , suffers very little change with time, but at  $25^{\circ}$  the conductivity rises from 95.44 to 122.97 in 34 mins., in consequence of the aq. solution of the salt. The subject was discussed by L. Tschugaeff. According to S. M. Jörgensen, the colour of the soln. changes to violet-red when it is boiled, in consequence of the formation of the chloro-aquonitrate; but on cooling, its green colour returns, in consequence of the re-formation of the dichloro-nitrate. Silver nitrate precipitates no silver chloride from the cold soln. A. Werner and A. Fröhlich prepared **cobaltic trans-dichlorobispropylenediaminenitrate**,  $[\text{Co pn}_2\text{Cl}_2]\text{NO}_3 \cdot \text{H}_2\text{O}$ , in matte green crystals, by triturating the corresponding chloride in a little water. The *monohydrate* loses its water of hydration in the desiccator. They also found that silver **cobaltic dichlorobispropylenediaminesulphonatonicrate**,  $2[\text{Co pn}_2\text{Cl}_2]\text{SO}_4 \cdot \text{Ag} \cdot \text{AgNO}_3$ , is formed, in malachite-green scales, on mixing cold, conc., aq. soln. of the component salts. The salt readily dissolves in water, and becomes bluish-

red on keeping—possibly owing to the formation of silver chloride, say  $2\text{Co}[\text{pn}_2\text{Cl}(\text{AgCl})]\text{SO}_4 \cdot \text{AgNO}_3$ . A. Werner obtained sparingly soluble **cobaltic dichlorobispyridinediamminonitrate**,  $[\text{Co}(\text{NH}_3)_2\text{py}_2\text{Cl}_2]\text{NO}_3$ , by adding nitric acid to a soln. of the chloride. C. Rix, and A. Werner and F. Chaussy prepared **cobaltic trans-dichloroethylenediaminediamminonitrate**,  $[\text{Co}(\text{NH}_3)_2\text{enCl}_2]\text{NO}_3$ , as a green precipitate, on adding, drop by drop, 1 : 1-nitric acid to a conc. soln. of the corresponding chloride. M. L. Ernsberger and W. R. Brode studied the absorption spectrum of **cobaltic chlorobromobisethylenediaminenitrate**.

S. M. Jörgensen<sup>15</sup> obtained **cobaltic dichloroaquotriamminonitrate**,  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})\text{Cl}_2]\text{NO}_3$ , by treating an ice-cold soln. of the hydrosulphate with dil. nitric acid; and A. Werner, by treating the chloride in a somewhat similar way. The dark green crystals are slightly dichroic—bluish-green and pale red—and the green, aq. soln. changes to blue when kept for some time. A. Werner and A. Grün obtained **cobaltic dichloroaquoethylenediamineamminonitrate**,  $[\text{Co}(\text{NH}_3)_2\text{en}(\text{H}_2\text{O})\text{Cl}_2]\text{NO}_3$ , by the action of nitric acid (1 : 4) on the chloride. The green crystals are freely soluble in water.

A. Werner prepared **cobaltic dichlorodiaquodiamminonitrate**,  $[\text{Co}(\text{NH}_3)_2(\text{H}_2\text{O})_2\text{Cl}_2]\text{NO}_3$ , by treating the hydrosulphate with cold, conc. nitric acid. The dark green, crystalline powder forms a green soln. with water, which soon becomes blue. The dry salt decomposes on keeping.

A. Werner and A. Wolberg prepared **cobaltic trans-dibromotetramminonitrate**,  $[\text{Co}(\text{NH}_3)_4\text{Br}_2]\text{NO}_3$ , by treating a cold soln. of the chloride with nitric acid. The pale green, prismatic crystals dissolve in water to form a soln. which soon changes into an aquo-salt. A. Werner and co-workers prepared **cobaltic cis-dibromobisethylenediaminenitrate**,  $[\text{Co en}_2\text{Br}_2]\text{NO}_3$ , in greyish-violet crystals, by adding sodium nitrate to a cold, sat., aq. soln. of the bromide. S. M. Jörgensen prepared **cobaltic trans-dibromobisethylenediaminenitrate**,  $[\text{Co en}_2\text{Br}_2]\text{NO}_3$ , by treating a soln. of the bromide, acidified with sulphuric acid, with dil. nitric acid (1 : 2). The rhombic, acicular crystals are isomorphous with those of the trans-dichloronitrate. E. Petersen, A. Werner and C. Herty, and W. D. Harkins and co-workers discussed the lowering of the f.p. of aq. soln., and the electrical conductivity. According to S. M. Jörgensen, the salt is sparingly soluble in water, and forms a yellowish-green soln.; the soln. gives precipitates with hydrochloroplatinic acid, sodium chloromercurate, and potassium dichromate. Silver nitrate gives a precipitate of silver bromide with an aged soln., but not with one freshly prepared. S. Berkman and H. Zocher, and G. Depold studied the magnetic constants of **cobaltic carbonatotetramminonitrate**,  $[\text{Co}(\text{NH}_3)_4(\text{CO}_3)]\text{NO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ .

E. Böhm<sup>16</sup> obtained **cobaltic fluohydroxytetramminonitrate**,  $[\text{Co}(\text{NH}_3)_4(\text{OH})\text{F}]\text{NO}_3$ , in purple-red, acicular or prismatic crystals, along with the hexamminofluonitrate, by the action of hydrofluoric acid and an excess of aq. ammonia, on cobaltous nitrate. H. Fischlin also prepared **cobaltic chlorohydroxybisethylenediaminenitrate**,  $[\text{Co en}_2(\text{OH})\text{Cl}]\text{NO}_3$ , by the action of lithium nitrate on the corresponding bromide—the *dextro*-salt, or the *lævo*-salt. The sp. rotation of the *dextro*-salt is  $[\alpha] = 530^\circ$ , and of the *lævo*-salt,  $-542^\circ$  in Na-light. J. Lifschitz studied the anomalous dispersion. A. Werner prepared dark violet needles of **cobaltic cis-bromochlorobisethylenediaminenitrate**,  $[\text{Co en}_2\text{ClBr}]\text{NO}_3$ , by treating a cold soln. of the bromide with ammonium nitrate. A. Werner and G. Tschernoff obtained the *dextro*-salt, and the *lævo*-salt by the action of conc. nitric acid on the corresponding camphorbromosulphonates. The dark grey powder, 45 mins. after being dissolved in water, becomes inactive. The sp. rotation of a soln. of the *dextro*-salt is  $[\alpha] = 144^\circ$ , and of the *lævo*-salt,  $-152^\circ$ . A. Werner also prepared **cobaltic trans-bromochlorobisethylenediaminenitrate**, by heating chloroaquobisethylenediaminebromide for some hours at  $110^\circ$ , triturating the mixture of violet cis- and green trans-bromochlorobromide with cold water and saturating the green soln. with ammonium nitrate. The violet cis-bromochlorobromide does not dissolve. The pale green plates are sparingly soluble in water.

A. Werner and A. Grün obtained pale green **cobaltic bromochloroaquotriamminonitrate**,  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})\text{ClBr}]\text{NO}_3$ , by adding conc. nitric acid to a cold,

aq. soln. of the bromide; and similarly with pale green **cobaltic bromochloro-aquoethylenediamineamminonitrate**,  $[\text{Co}(\text{NH}_3)_5\text{en}(\text{H}_2\text{O})\text{ClBr}]\text{NO}_3$ .

R. Luther and H. Frieser studied the decomposition of **cobaltic trinitratotriammine**,  $[\text{Co}(\text{NO}_3)_3(\text{NH}_3)_3]$ , in acidic soln., in light and in darkness.

### *Complexes with Two or More Carbon Atoms*

E. Frémy<sup>17</sup> prepared **cobaltic peroxo-decamminotetranitrate**,  $[(\text{NH}_3)_5\text{Co}-\text{O}_2-\text{Co}(\text{NH}_3)_5](\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$ , in dark brown prisms, by the aerial oxidation of a conc. ammoniacal soln. of cobaltous nitrate. The salt was also prepared by G. Vortmann, C. Schwenk, and O. W. Gibbs. A. Werner and A. Mylius recommend the following process for preparing what was formerly called *oxycobaltamine nitrate*:

Cobalt nitrate (200 grms.) is dissolved in water (250 grms.), the boiling solution poured into ammonia (850 grms., sp. gr. = 0.927), and the mixture heated for about 5 minutes; when cold, the mixture is filtered and treated with a slow current of air as long as a thick, crystalline precipitate is formed. The crystals of the peroxo-nitrate are collected, washed with ammonia and alcohol, and dried by pressing between filter-paper.

The brown crystals sometimes become green when dried; and when formed in the presence of ammonium nitrate, the prisms are dark olive-green, almost black. A. Werner and A. Mylius, and A. Mylius observed that the salt decomposes at  $110^\circ$ , and G. Vortmann, that it explodes at  $200^\circ$ . E. Feytis gave  $0.092 \times 10^{-6}$  mass unit for the magnetic susceptibility. E. Frémy observed that the salt is decomposed by sulphuric acid, potash-lye, or water, in the cold, and oxygen is given off. G. Vortmann noted that it decolorizes soln. of permanganates. According to A. Werner and A. Mylius, after heating at  $110^\circ$  until the weight is constant, the product, when treated with a small quantity of water, and the brown filtrate mixed with conc. hydrochloric acid, yields, after a time, a brown precipitate consisting of a mixture of melanocobalt chloride, hexamminochloride, and aquopentamminochloride. The melanocobalt chloride, which is formed in small quantities only, remains undissolved when the mixture is treated with water. The soln. containing the other two salts is boiled with hydrochloric acid, when the chloropentamminochloride is precipitated from the hot soln., and the hexamminochloride separates on cooling. This operation must be repeated several times in order to effect a complete separation. When the brown, aq. soln. obtained from the product from the peroxo-decamminonitrate, after heating at  $110^\circ$ , is treated with nitric instead of with hydrochloric acid, hexamminonitrate is obtained, and on adding hydrochloric acid to the filtrate from this salt, chloropentamminochloride is precipitated. G. Vortmann obtained **cobaltic peroxo-decamminohydrionitrate**,  $[\text{Co}_2(\text{O}_2)(\text{NH}_3)_{10}](\text{NO}_3)_4 \cdot \text{HNO}_3 \cdot 3\text{H}_2\text{O}$ , by half an hour's action of conc. nitric acid on the normal nitrate. The brownish powder is very unstable. He also prepared **cobaltic peroxo-decamminohydrochloronitrate**,  $[\text{Co}_2(\text{O}_2)(\text{NH}_3)_{10}](\text{NO}_3)_2 \cdot \text{Cl}_2 \cdot 4\text{HCl} \cdot \text{H}_2\text{O}$ , by the action of conc. hydrochloric acid on the nitrate. The brownish-violet crystals are very unstable. By the action of nitric acid on the sulphate, G. Vortmann also prepared **cobaltic peroxo-decamminohydrosulphatonitrate**,  $[\text{Co}_2(\text{O}_2)(\text{NH}_3)_{10}](\text{SO}_4)_2 \cdot 4\text{HNO}_3 \cdot \text{H}_2\text{O}$ , in brownish-violet, unstable crystals.

G. Vortmann prepared what was formerly called *anhydroxycobaltamine nitrate*, or **cobaltic peroxo-decamminopentanitrate**,  $[(\text{NH}_3)_5\text{Co}-\text{O}_2-\text{Co}(\text{NH}_3)_5](\text{NO}_3)_5$ , by dissolving the tetranitrate, just described, in warm nitric acid (1 : 1), and cooling, and re-crystallizing from water acidulated with nitric acid. A. Werner and A. Mylius recommended the following process:

Fifty grms. of cobalt carbonate, dissolved in the necessary quantity of dil. nitric acid, are mixed with 200 grms. of ammonium nitrate, and filtered, mixed with 600 c.c. of ammonia (20 per cent.), and treated with a current of air for 26 to 48 hours, until the soln. no longer smells strongly of ammonia. The black soln., which contains crystals of E. Frémy's tetranitrate, is evaporated to a magma in a current of air, mixed with nitric acid, and the salt separated by filtration, and washed with cold, dil. nitric acid until the filtrate is

colourless. The pentanitrate is completely insoluble in dil. nitric acid, whereas it is quickly decomposed by pure water. It crystallizes from hot, dil. nitric acid (20 c.c. acid to 1000 c.c. water) in black, lustrous needles.

S. M. Jörgensen used a similar process. G. Vortmann observed that the salt decomposes with the evolution of oxygen. A. Werner and A. Mylius found that when treated with hydrochloric acid, the salt forms chloropentamminochloride; sulphurous acid converts it into aquopentamminonitrate; and potassium cyanide forms a complex cyanide with the evolution of ammonia and hydrogen cyanide. G. Vortmann observed that if the corresponding chloride is treated with dil. hydrochloric acid, **cobaltic peroxo-decamminochlorotetranitrate**,  $[\text{Co}_2(\text{O}_2)(\text{NH}_3)_{10}]\text{Cl}(\text{NO}_3)_4 \cdot \text{H}_2\text{O}$ , in leek-green crystals is formed; and with conc. hydrochloric acid, **cobaltic peroxo-decamminotrichlorodinitrate**,  $[\text{Co}_2(\text{O}_2)(\text{NH}_3)_{10}]\text{Cl}_3(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ , is formed, also in leek-green crystals. When peroxo-decamminotetranitrate is treated with sulphuric acid (1:1), and cooled, **cobaltic peroxo-decamminonitratodisulphate**,  $[\text{Co}_2(\text{O}_2)(\text{NH}_3)_{10}](\text{SO}_4)_2\text{NO}_3 \cdot \text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ , is formed in green crystals, which are sparingly soluble in water, and become matte at  $110^\circ$ . A. Werner prepared **cobaltic trichlorohydroxy-peroxohexamminonitrate**,  $[\text{Cl}_2(\text{NH}_3)_3\text{O}_2\text{Co}(\text{NH}_3)_3(\text{OH})\text{Cl}]\text{NO}_3$ , by treating the corresponding chloride with conc. nitric acid.

A. Werner and co-workers prepared what they called **cobaltic diozotriimidodecamminonitrate**,  $[\text{Co}_4(\text{O}_2)_2(\text{NH}_3)_3(\text{NH}_3)_{10}](\text{NO}_3)_5 \cdot 5\text{H}_2\text{O}$ , by treating a soln. of the chloride in dil. nitric acid with silver nitrate. The product furnishes black, tetrahedral crystals. When treated with warm, conc. nitric acid, it yields cobaltous salts and a bright red salt which, when treated with hydrochloric acid, is converted into the dichloroaquotriamminochloride. When treated with nitrous acid, it yields an imidohexammine salt, probably nitratotriaquaimidoexaminonitrate, and the mother-liquors of this salt, when treated with hydrochloric acid, yield the dichlorotetramminochloride and a dark-coloured salt of unknown composition.

A. Werner and co-workers obtained **cobaltic sulphatoimino-octamminonitrate**,  $[(\text{NH}_3)_4\text{Co}=(\text{NH})(\text{SO}_4)=\text{Co}(\text{NH}_3)_4](\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , in pale violet crystals, by treating sulphato- $\mu$ -amino-octamminonitrate with conc. ammonia. A. Werner prepared **cobaltic  $\mu$ -aminodecamminonitrate**,  $[(\text{NH}_3)_5\text{Co}-\text{NH}_2 \cdots \text{Co}(\text{NH}_3)_5](\text{NO}_3)_5$ , when  $\mu$ -amino-ol-octamminonitrate is treated with cold, conc. nitric acid. As indicated below, it forms nitratoaquo- $\mu$ -amino-octamminonitrate, and this is converted into  $\mu$ -amino-decamminonitrate when it is gradually added to well-stirred, liquid ammonia—a small quantity of the initial salt is at the same time regenerated. The same compound is produced by treating chloroaquo- $\mu$ -amino-octamminochloride with conc. nitric acid, and dissolving the product of the reaction, chloronitratato- $\mu$ -amino-octamminonitrate, in liquid ammonia, and, after evaporating off the ammonia, the residue is covered with water, and heated on a water-bath until the greater part has dissolved. The insoluble part is filtered from the hot soln., and re-crystallized from water containing acetic acid, when long, red needles of the  $\mu$ -amino-decamminonitrate are formed. The constitution of this salt was determined independently of the octammine series, as chloropentammine and hexammine salts are obtained by the action of a mixture of hydrochloric and sulphuric acids, from which the deduction is made that 5 mols. of ammonia are attached to each of the cobalt atoms, thus:  $[(\text{NH}_3)_5\text{Co} \cdot \text{NH}_2 \cdot \text{Co}(\text{NH}_3)_5]\text{Cl}_5 + \text{HCl} = [\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2 + [\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ . That the decammine salt is not an imino-derivative of the type,  $[(\text{NH}_3)_5\text{Co} \cdot \text{NH}(\text{HCl}) \cdot \text{Co}(\text{NH}_3)_5]\text{Cl}_4$ , is shown by its behaviour towards alkalis, the elements of hydrogen chloride not being withdrawn. The bluish-red needles are soluble in 200 grms. of water per gram of salt, and the soln. has a neutral reaction; it is precipitated almost quantitatively from its aq. soln. by nitric acid; and it is not decomposed by boiling nitric acid. A. Werner and A. Baselli prepared **cobaltic nitratato-aquo- $\mu$ -amino-octamminonitrate**,  $[(\text{H}_2\text{O})(\text{NH}_3)_4\text{Co} \cdots \text{NH}_2 - \text{Co}(\text{NH}_3)_4(\text{NO}_3)](\text{NO}_3)_4$ , by triturating 5 grms. of  $\mu$ -amino-ol-octamminonitrate with 15 c.c. of cold, conc. nitric acid, allowing the mixture to stand for 12 hrs., draining the crystals on a porous plate, and washing several times with

alcohol. The violet powder is converted by liquid ammonia into the  $\mu$ -amino-decamminonitrate. The aq. soln. reacts acidic, since, by aqation,  $[\text{Co}_2(\text{NH}_2)(\text{NH}_3)_8(\text{H}_2\text{O})](\text{NO}_3)_5$ , is formed. A. Werner prepared **cobaltic chloronitrato- $\mu$ -amino-octamminonitrate**,  $[\text{Cl}(\text{NH}_3)_4\text{Co}-\text{NH}_2\cdots\text{Co}(\text{NH}_3)_4(\text{NO}_3)](\text{NO}_3)_3$ , by treating a freshly-prepared soln. of chloroaquo- $\mu$ -amino-octamminochloride with conc. nitric acid. The greyish-violet needles readily dissolve in water; the freshly-prepared soln. gives no precipitate with silver nitrate, but when the soln. has aged for a few hours, it gives a precipitate of silver chloride, indicating that some aqation has taken place. Dil. sulphuric acid precipitates  $\mu$ -amino-ol-octamminosulphate from the warm soln. of the nitrate. A. Werner, and I. Fürstenberg prepared **cobaltic tetrabromo- $\mu$ -amino-hexamminonitrate**,  $[\text{Br}_2(\text{NH}_3)_3\text{Co}-\text{NH}_2\cdots\text{Co}(\text{NH}_3)_3\text{Br}_2]\text{NO}_3 \cdot 2\text{H}_2\text{O}$ , by treating the bromide with nitric acid (1:1). The brownish-green powder loses 2 mols. of water at  $80^\circ$ . A. Werner obtained **cobaltic trichloronitrate- $\mu$ -amino-hexamminonitrate**,  $[\text{Cl}_2(\text{NH}_3)_3\text{Co}-\text{NH}_2\cdots\text{Co}(\text{NH}_3)_3(\text{NO}_3)\text{Cl}]\text{NO}_3$ , in violet-black crystals, by the action of conc. nitric acid on trichloroaquo- $\mu$ -amino-hexamminochloride, and precipitating the salt from the cold, aq. soln. by conc. nitric acid.

According to A. Werner and A. Baselli, **cobaltic sulphato- $\mu$ -amino-octamminonitrate**,  $[(\text{NH}_3)_4\text{Co}=(\text{NH}_2)(\text{SO}_4)\cdots\text{Co}(\text{NH}_3)_4](\text{NO}_3)_3$ , can be obtained by treating cobalt with fuming nitric acid, and, after allowing the mixture to remain for an hour, washing the violet precipitate with water, this operation being repeated three times; the precipitate is then washed with water until the wash-water becomes violet-red, and the product re-crystallized from dilute nitric acid; it cannot, however, be completely purified by this means. In order to obtain the pure salt, the crude product is converted into the chloronitrate, dissolved in the smallest quantity of water, and precipitated with nitric acid; it crystallizes in small, violet leaflets, is only sparingly soluble in cold water, and decomposes when heated on the water-bath, especially in the absence of free acid; but the dry salt is stable at  $110^\circ$ . The sulphuric acid contained in this salt cannot be detected by a direct method. A. Werner and A. Baselli also prepared **cobaltic sulphato- $\mu$ -amino-octamminodichloronitrate**,  $[(\text{NH}_3)_4\text{Co}=(\text{NH}_2)(\text{SO}_4)\cdots\text{Co}(\text{NH}_3)_4](\text{NO}_3)\text{Cl}_2$ , by dissolving the crude nitrate in hydrochloric acid on the water-bath, filtering as quickly as possible, and cooling the filtrate with ice and salt, the crystalline product being washed free from acid with water and with alcohol, and dried on a porous plate over sulphuric acid. It crystallizes in slender, microscopic, violet needles, easily soluble in water, and when warmed with hydrochloric acid and water, is converted into the sulphato- $\mu$ -amino-octammine salt. The aq. soln. gives characteristic precipitates with several metallic salts; for example, the sat., aq. soln. gives precipitates with sodium and potassium iodides and bromides, with potassium ferrocyanide and ferricyanide, with auric chloride, with hydrochloroplatinic acid, and with oxalic acid. A. Werner prepared optically inactive or racemic **cobaltic sulphato- $\mu$ -amino-quaterethylenediaminenitrate**,  $[\text{en}_2\text{Co}=(\text{NH}_2)(\text{SO}_4)\cdots\text{Co en}_2](\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$ , in red prisms, from the  $\mu$ -amino-peroxo-quaterethylenediaminenitrate, by dissolution in conc. sulphuric acid; this is attended by the development of heat, and, on cooling, reddish-brown crystals separate. Further treatment with sulphur dioxide gives a red salt, from the aq. soln. of which concentrated nitric acid precipitates the required nitrate as light red needles. The optically active *dextro*-salt is obtained by treating *laevo*- $\mu$ -amino-peroxo-quaterethylenediaminenitrate with sulphurous acid, as just indicated for the optically inactive salt. The sp. rotation of a 0.125 per cent. aq. soln. is  $[\alpha]=200^\circ$ .

A. Werner prepared **cobaltic diol-octamminonitrate**,  $[(\text{NH}_3)_4\text{Co}\cdots(\text{OH})_2\cdots\text{Co}(\text{NH}_3)_4](\text{NO}_3)_4$ , as a bright carmine-red crystalline powder, by adding 25 c.c. of a cold, sat. soln. of sodium nitrate to a soln. of 3 grms. of the corresponding chloride in 140 c.c. of water, and reprecipitating the salt by sodium nitrate from its aq. soln. A. Werner and J. Rapiort obtained **cobaltic diol-quaterethylenediaminenitrate**,  $[\text{en}_2\text{Co}\cdots(\text{OH})_2\cdots\text{Co en}_2](\text{NO}_3)_4$ , by similarly treating an aq. soln. of the corre-



sponding bromide. The purple, crystalline powder is readily soluble in water. E. Rosenbohm found the magnetic susceptibility to be  $-0.193 \times 10^{-6}$  mass unit; and L. C. Jackson studied the magnetic properties of the salt. A. Werner obtained **cobaltic dinitrato-diol-hexamminonitrate**,  $[(\text{NO}_3)(\text{NH}_3)_3\text{Co} \cdots (\text{OH})_2 \cdots \text{Co}(\text{NH}_3)_3(\text{NO}_3)](\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , by treating an ice-cold soln. of triol-hexamminosulphate in 8 c.c. of water, with 5 c.c. of cold nitric acid (1:1), and stirring the mixture for 5 to 10 mins. The crystals are drained, washed with alcohol and ether; and purified by adding nitric acid to the aq. soln. The pale violet scales form a bluish-red soln. with water; the aq. soln. reacts neutral, but with ageing, the soln. becomes acidic, owing to aquation.

A. Werner prepared **cobaltic hydroxyaquo-peroxo-ol-hexamminonitrate**,  $[(\text{OH})(\text{NH}_3)_3\text{Co}=(\text{OH})(\text{O}_2) \cdots \text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})](\text{NO}_3)_3$ , by triturating the corresponding sulphate with ammonium nitrate and water acidulated with acetic acid, precipitating from the filtrate with ammonium nitrate, and purifying by adding alcohol to the aq. soln. It is also present amongst the products obtained by treating cobalt melanochloride with silver nitrate. The dark brown, tabular crystals form, with water, a brown soln. having an alkaline reaction. If a cold, aq. soln., acidified with acetic acid, be treated with conc. hydrochloric acid, the chloride of the series is not obtained, for the ol-bridge is broken, and trichlorohydroxy-peroxo-hexamminochloride is formed—*vide supra*.

A. Werner obtained **cobaltic  $\mu$ -imino-peroxo-quaterethylenediaminenitrate**,  $[\text{en}_2\text{Co}=(\text{O}_2)(\text{NH})=\text{Co en}_2](\text{NO}_3)_3$ , in brown needles, by triturating the iodide with water and the theoretical amount of silver nitrate, and evaporating the filtrate over sulphuric acid. The aq. soln. gives a precipitate of silver nitrate. The addition compound, **silver cobaltic  $\mu$ -imino-peroxo-quaterethylenediaminenitrate**,  $3[\text{Co}_2(\text{O}_2)(\text{NH})\text{en}_4](\text{NO}_3)_3 \cdot 5\text{AgNO}_3$ , was obtained in dark brown crystals; and similarly, copper nitrate furnishes **copper cobaltic  $\mu$ -imino-peroxo-quaterethylenediaminenitrate**, in apple-green crystals; and mercuric chloride gives bright red crystals of **mercuric cobaltic  $\mu$ -imino-peroxo-quaterethylenediaminechloronitrate**.

A. Werner obtained **cobaltic  $\mu$ -amino-peroxo-quaterethylenediaminenitrate**,  $[\text{en}_2\text{Co}=(\text{O}_2)(\text{NH}.\text{HNO})=\text{Co en}_2](\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$ , by triturating  $\mu$ -amino-peroxo-octamminonitrate with 10 per cent. ethylenediamine, and boiling the mixture until ammonia is no longer given off. The cold, brown liquor is mixed with nitric acid, added drop by drop, until the colour becomes red, and it is then cooled in a freezing mixture. The red, crystalline powder is washed with alcohol and ether. The salt in soln. changes into the green isomeric  $\mu$ -amino-peroxo-quaterethylenediaminenitrate.

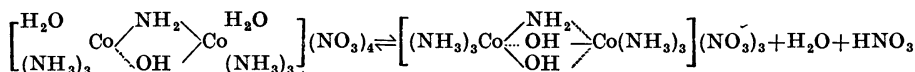
A. Werner and F. Beddow, and C. Schwenk prepared **cobaltic  $\mu$ -amino-peroxo-octamminonitrate**,  $[(\text{NH}_3)_4\text{Co}=(\text{NH}_2)(\text{O}_2) \cdots \text{Co}(\text{NH}_3)_4](\text{NO}_3)_4$ , which they regarded as a *dihydrate*, by treating cobalt fuscousulphate with conc. nitric acid; on diluting with water, a dark green soln. is obtained, and a violet-red, insoluble salt; on mixing the aq. soln. with conc. nitric acid, the nitrate is precipitated. It crystallizes from acidified water in dark green prisms; it is very soluble in water; and it decomposes in neutral solns. with the evolution of ammonia and the precipitation of cobalt oxide; when heated at  $100^\circ$ , it does not give off its water of crystallization. They also said that a *hexahydrate* can be obtained by precipitating a well-cooled soln. of the preceding salt with a small quantity of nitric acid; and it crystallizes in silky, olive-green needles. When this nitrate is heated with an aq. soln. of ammonium carbonate, a dark brown salt is deposited, which has the composition of a basic tetrammine salt. It is sparingly soluble in cold water, easily so in warm water acidified with acetic acid, and crystallizes in black, flat prisms; a salt which is probably identical with this is obtained on treating the nitrate with ammonia. Neither A. Werner and A. Baselli, nor A. Werner and A. Grün could prepare these hydrates; the anhydrous salt was always obtained. The peroxo-salt is reduced by potassium iodide, or by sulphurous or nitrous acids. The central group is so stable that when this nitrate is warmed with 10 per cent. ethylenediamine, all the  $\text{NH}_3$ -groups can be displaced to furnish **cobaltic  $\mu$ -amino-peroxo-quaterethylenediaminenitrate**,  $[\text{en}_2\text{Co}=(\text{NH}_2)(\text{O}_2) \cdots \text{Co en}_2](\text{NO}_3)_4$ , in green needles. According to A. Werner and co-workers, if a well-cooled soln. of the optically-

active camphorbromosulphonates of the series be treated with conc. nitric acid and then with alcohol, the *dextro-salt*, and the *laevo-salt* can be obtained as pale olive-green, crystalline powders, very soluble in water. The sp. rotations of 0.125 per cent. aq. soln. are  $[\alpha] = \pm 920^\circ$ .

A. Werner prepared symmetrical—*vide supra*, the corresponding chlorides—**cobaltic dichloro- $\mu$ -amino-peroxo-hexamminonitrate**,  $[\text{Cl}(\text{NH}_3)_3\text{Co}=(\text{NH}_2)(\text{O}_2)\cdots\text{Co}(\text{NH}_3)_3\text{Cl}](\text{NO}_3)_2$ , by triturating the chloride several times with conc. nitric acid. The black, microcrystalline powder is sparingly soluble in water.

A. Werner obtained **cobaltic  $\mu$ -amino-ol-octamminonitrate**,  $[(\text{NH}_3)_4\text{Co}=(\text{NH}_2)(\text{OH})\cdots\text{Co}(\text{NH}_3)_4](\text{NO}_3)_4$ , by acting on the corresponding chloride with silver nitrate, and precipitating from the filtered soln. with nitric acid. The raspberry-red prisms, needles, or scales are stable at  $80^\circ$ ; 100 grms. of water dissolve 0.833 grm. of the salt at room temp., but the neutral soln. is unstable. Conc. hydrochloric acid forms chloroaquo- $\mu$ -amino-octamminochloride; and triturating with ammonium bromide furnishes the bromide.

A. Werner and co-workers—I. Fürstenberg, F. Steinitzer, and A. Mylius—prepared **cobaltic diaquo- $\mu$ -amino-ol-hexamminonitrate**,  $[(\text{H}_2\text{O})(\text{NH}_3)_3\text{Co}\cdots(\text{NH}_2)(\text{OH})\cdots(\text{NH}_3)_3(\text{H}_2\text{O})](\text{NO}_3)_4\cdot 2\text{H}_2\text{O}$ . A mixture of 650 grms. of cobalt chloride with 400 c.c. of water and 2 litres of 25 per cent. ammonia is heated to boiling, filtered from the precipitated cobalt oxide, and exposed to the air for 48 hrs. The resulting brownish-red solution is filtered from the crystals which have deposited, and mixed with 3 litres of concentrated hydrochloric acid. The resulting brownish-red precipitate is quickly collected and extracted with cold water until it becomes pure grey in colour and the wash-water is coloured a brownish-violet. One kilogram of cobalt chloride gives about 60 grms. of melano-chloride. The aq. soln. is acidic, owing to the hydration represented as a balanced reaction by the equation:



so that both the ol- and the diol-salts are precipitated from aq. soln. Potassium bromide or iodide gives the corresponding salts of  $\mu$ -amino-diol-hexammine; warm hydrochloric acid gives trichloro-aquo- $\mu$ -amino-hexamminochloride; warm hydrobromic acid forms tetrabromo- $\mu$ -amino-hexamminobromide; and warm acetic acid forms the  $\mu$ -amino-ol-acetatohexammine. The salt is precipitated from a cold, aq. soln. by conc. nitric acid, or ammonium nitrate; and, according to A. Werner and co-workers, hot, conc. nitric acid yields **cobaltic nitratoaquo- $\mu$ -amino-ol-hexamminonitrate**,  $[(\text{H}_2\text{O})(\text{NH}_3)_3\text{Co}\cdots(\text{NH}_2)(\text{OH})\cdots\text{Co}(\text{NH}_3)_3(\text{NO}_3)](\text{NO}_3)_3\cdot 2\text{H}_2\text{O}$ . This salt was prepared by A. Werner, by dissolving a gram of diaquo- $\mu$ -amino-ol-hexamminonitrate in 7 c.c. of hot water to which a few drops of nitric acid have been added, 18 c.c. of conc. nitric acid are added to the well-cooled soln., and in a few minutes, yellowish-brown, flat needles separate out. The salt can be re-crystallized from warm water by the addition of nitric acid. Liquid ammonia converts it into  $\mu$ -amino-ol-octamminonitrate.

A. Werner prepared **cobaltic triol-hexamminonitrate**,  $[(\text{NH}_3)_3\text{Co}\cdots(\text{OH})_3\cdots\text{Co}(\text{NH}_3)_3](\text{NO}_3)_3\cdot 2\text{H}_2\text{O}$ , by treating an ice-cold, conc., aq. soln. of the chloride or bromide with sodium nitrate, and re-crystallizing from a little water by adding sodium nitrate. The red prisms of the *dihydrate* lost the water of hydration over sulphuric acid, phosphorus pentoxide, or at  $60^\circ$ ; 100 grms. of water dissolve 8.33 grm. of the salt at room temp.

According to A. Pieroni and A. Pinotti, red, acicular crystals are precipitated when nitric acid is added to a soln. of diol-peroxo-sexiesallylaminechloride, and W. R. Bucknall and W. Wardlaw found that **cobaltic diol-peroxo-sexiesallylaminonitrate**,  $[(\text{C}_3\text{H}_5\text{NH}_2)_3\text{Co}\cdots(\text{O}_2)(\text{OH})\cdots\text{Co}(\text{C}_3\text{H}_5\text{NH}_2)_3](\text{NO}_3)$ , can be prepared by the addition of about 1 c.c. of nitric acid to 20 c.c. of a soln. of the complex

chloride (2 grms.), and freed from acid by washing with cold water, in which it is slightly soluble; the filtered substance can be air-dried on a porous plate. It contained no chlorine, and when it was moistened with sulphuric acid, nitric acid was liberated. It was slightly soluble in cold water, and on standing, or by warming, hydrolysis occurred, with the precipitation of hydroxide. Warming with sodium hydroxide caused the evolution of allylamine, and by distillation with sodium hydroxide and Devarda's alloy, the nitrate groups are reduced to ammonia. The nitrate is hydrolyzed by boiling water, but the presence of nitric acid retards the hydrolysis; if the conc. of the nitric acid is too great, the salt is dissolved and the complex ion broken down.

According to A. Werner, **cobaltic  $\mu$ -amino-di-ol-hexamminonitrate**,  $[(\text{NH}_3)_3\text{Co} \cdots (\text{NH}_2)(\text{OH})_2 \cdots \text{Co}(\text{NH}_3)_3](\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$ , is formed by the action of a conc. soln. of silver nitrate on the corresponding iodide, and the subsequent addition of alcohol. The red crystals furnish an aq. soln. with a neutral reaction. A. Werner and co-workers—A. Baselli, F. Steinitzer and K. Rücker, and F. M. Grigorieff—obtained **cobaltic  $\mu$ -amino-ol-peroxo-hexamminonitrate**,  $[(\text{NH}_3)_3\text{Co} \cdots (\text{NH}_2)_2(\text{OH})(\text{O}_2) \cdots \text{Co}(\text{NH}_3)_3](\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ , as a by-product in the action of silver nitrate on the melanochloride. It is also produced when the corresponding bromide is treated with the theoretical quantity of silver nitrate in cold soln., and the filtrate treated with alcohol. The green scales form a greenish-brown soln., which becomes red when reduced with sulphurous acid; hydrochloric and hydrobromic acids break down the ol-bridge to form the dichlorochloride, or dibromo-bromide; and fuming nitric acid forms trinitratotriamine.

S. M. Jørgensen observed that **cobaltic hexol-dodecamminonitrate**,  $[\text{Co}\{(\text{OH})_2=\text{Co}(\text{NH}_3)_4\}_3](\text{NO}_3)_6$ , is precipitated, in greyish-brown, acicular crystals when a soln. of the corresponding chloride is treated with dil. nitric acid, and the product washed with alcohol and ether, and dried over sulphuric acid. The aq. soln. has a neutral reaction, and behaves towards general reagents like a soln. of the chloride. A. Werner found that **cobaltic hexol-sexiesethylenediaminenitrate**,  $[\text{Co}\{(\text{OH})_2=\text{Co}(\text{en})_2\}_3](\text{NO}_3)_6 \cdot 3\text{H}_2\text{O}$ , is formed when a soln. of cobalt nitrate and of ethylenediamine is submitted to atmospheric oxidation; it crystallizes in long, dark brown needles, yields cis-diaquobisethylenediaminecobaltic halide by solution in conc. hydrochloric or hydrobromic acid, trans-dichlorodietthylenediaminechloride by evaporation with dil. hydrochloric acid, and cis-hydroxo-aquobisethylenediaminenitrate by treatment with potassium hydroxide. The 10 per cent. aq. soln. gives crystalline precipitates with potassium bromide, iodide, and thiocyanate, with sodium nitrate, and with platonic chloride; and no precipitate with sodium nitrite, sulphate, and dithionate, or with ammonium chloride. E. Schmidt obtained this salt. The complex with gum arabic was studied by H. G. B. de Jong and J. Lens.

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## § 29. Cobaltous Phosphates

According to H. Rose,<sup>1</sup> A. Salvétat, W. J. Russell, and A. Terreil, when a soln. of a cobaltous salt is treated with sodium hydrophosphate, reddish-violet flakes are formed, and when heated in hydrogen gas, it furnishes cobalt tritridiphosphate, so that the salt probably contains the molar proportion  $\text{CoO} : \text{P}_2\text{O}_5 = 3 : 1$ , that is, **cobaltous orthophosphate**,  $\text{Co}_3(\text{PO}_4)_2$ . A. Reynoso obtained small, octahedral, rose-red crystals by heating the pyrophosphate with water, in a sealed tube, for 5 or 6 hrs. at  $280^\circ$  to  $300^\circ$ ; and F. Ephraim and C. Rossetti obtained rectangular plates by crystallization from a soln. containing more than a mol. of  $\text{P}_2\text{O}_5$  to 3 mols. of  $\text{CoO}$ . E. Birk and W. Biltz observed that the dehydrated phosphate has the sp. gr. 2.587 at  $25^\circ/4^\circ$ , and the mol. vol. 141.8. F. de Boer studied the K-series of the X-ray absorption spectrum; and E. F. Herroun, its magnetic properties. The violet-salt forms a deep red soln. with an excess of phosphoric acid; it dissolves in aq. ammonia, and in a soln. of ammonium chloride or nitrate. A. Salvétat observed that the reddish-violet salt becomes violet-blue when heated; and J. B. Senderens noted that it is not attacked by sulphur in boiling water. E. Birk and W. Biltz observed that the dehydrated salt is not attacked by ammonia under press.; A. Naumann, that it is insoluble

in methyl acetate; and J. A. Hedvall and J. Heuberger studied the reactions with heated alkaline earth oxides. According to H. Debray, the *dihydrate*,  $\text{Co}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ , is formed when hydrated cobaltous hydrophosphate is heated with water, or with cobaltous nitrate, in a sealed tube, at  $250^\circ$ ; or, according to G. Chancel, when hydrated ammonium cobaltous phosphate is boiled with water. H. Bassett and W. L. Bedwell obtained the *tetrahydrate*,  $\text{Co}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ . A. Reynoso obtained the *octohydrate*,  $\text{Co}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ , by adding alcohol to a soln. of the dihydrophosphate; H. Bassett and W. L. Bedwell also prepared this salt. According to M. Reitler, the commercial salt is the octohydrate. E. Birk and W. Biltz observed that if the flocculent precipitate of cobalt orthophosphate is allowed to stand in the mother-liquor, it forms the crystalline octohydrate. The sp. gr. is  $2.769$  at  $25^\circ/4^\circ$ ; and the mol. vol.,  $184.6$ . The hydrate loses all its combined water at  $200^\circ$ . N. S. Kurnakoff and I. A. Andreevsky found that the dehydration curves have breaks at  $110^\circ$ ,  $190^\circ$ , and  $270^\circ$ . According to E. Birk and W. Biltz, the hydrate is easily soluble in conc. aq. ammonia. R. F. Weinland and co-workers obtained a complex salt with pyridine, namely,  $\text{Co}_3(\text{PO}_4)_2 \cdot \text{C}_5\text{H}_5\text{N} \cdot 6\text{H}_2\text{O}$ , as a violet-blue powder. J. A. Hedvall and E. Norström studied the reactions with the oxides of the alkaline earths. W. Muthmann and H. Heramhof tried cobalt phosphate as a pigment for porcelain.

H. Debray obtained **ammonium cobaltous orthophosphate**,  $(\text{NH}_4)\text{CoPO}_4 \cdot 6\text{H}_2\text{O}$ , or  $(\text{NH}_4)_3\text{PO}_4 \cdot \text{Co}_3(\text{PO}_4)_2 \cdot 18\text{H}_2\text{O}$ , as a *hexahydrate*, by the action of an excess of ammonium phosphate on a soln. of a cobalt salt at  $80^\circ$ ; M. Porumbaru, by heating neutral or acid cobaltic aquopentamminopyrophosphate, in a sealed tube, at  $225^\circ$ ; and H. D. Dakin obtained the *monohydrate*, by evaporating to dryness, at  $100^\circ$  to  $105^\circ$ , a soln., of a cobalt salt mixed with ammonium hydrophosphate. The monohydrate furnishes violet crystals which do not decompose in boiling water, and which do not lose ammonia at  $110^\circ$ . The subject was discussed by A. Brand, P. Dirvell, H. Bassett and W. L. Bedwell, H. Behrens, and O. Richter. G. Chancel also described rose-red crystals of the *dodecahydrate* obtained by treating a cold soln. of a cobalt salt with an excess of ammonium phosphate, and allowing the bluish-violet, gelatinous precipitate to stand in contact with its mother-liquor for some time. The crystals partially decompose at  $100^\circ$  into cobaltous and ammonium phosphates.

L. Ouvrard melted cobalt oxide with potassium pyrophosphate or hydrophosphate, potassium metaphosphate or orthophosphate with an excess of cobalt oxide, or cobaltous orthophosphate and potassium chloride, and obtained **potassium cobaltous orthophosphate**,  $\text{KCoPO}_4$ , or  $\text{K}_3\text{PO}_4 \cdot \text{Co}_3(\text{PO}_4)_2$ , and H. Grandeau obtained the same salt by heating cobaltous orthophosphate with potassium sulphate between  $800^\circ$  and  $1000^\circ$ , and washing the product with water. The blue, rhombic crystals have the sp. gr.  $3.5$  at  $20^\circ$ , and are easily soluble in acids. If the temp. of preparation is in the vicinity of  $1400^\circ$ , some higher oxide of cobalt is formed. L. Ouvrard melted potassium metaphosphate with cobalt oxide and obtained rose-red, monoclinic crystals of potassium cobaltous phosphate,  $\text{K}_3\text{PO}_4 \cdot 3\text{KCoPO}_4$ , or  $2\text{K}_3\text{PO}_4 \cdot \text{Co}_3(\text{PO}_4)_2$ , of sp. gr.  $2.9$  at  $20^\circ$ . The presence of potassium chloride favours crystallization. The crystals are soluble in acids. L. Ouvrard also obtained **sodium cobaltous orthophosphate** by fusing together sodium metaphosphate with an excess of cobalt oxide in the presence of sodium chloride; and also by fusing sodium pyrophosphate with an excess of cobalt oxide; or cobaltous orthophosphate with an excess of sodium chloride. The rhombic prisms are isomorphous with those of the corresponding zinc salt, and have a sp. gr.  $3.6$  at  $20^\circ$ . By melting together sodium pyrophosphate with a small proportion of cobalt oxide; or sodium orthophosphate and cobalt oxide, crystals of  $\text{Na}_3\text{PO}_4 \cdot \text{NaCoPO}_4$ , or  $\text{Na}_4\text{Co}(\text{PO}_4)_2$ , isomorphous with those of the corresponding zinc salt, are obtained. Their sp. gr. is  $2.5$  at  $20^\circ$ .

J. G. Gentile obtained **zinc cobaltous orthophosphate**,  $3\text{Zn}_3(\text{PO}_4)_2 \cdot \text{Co}_3(\text{PO}_4)_2 \cdot 12\text{H}_2\text{O}$ , by adding a mixed soln. of zinc and cobalt sulphates to an excess of a

soln. of sodium hydrophosphate, the green precipitate which soon becomes blue. An excess of zinc sulphate yields a green precipitate, and an excess of cobalt sulphate, a blue one. J. G. Gentile described the use of the mixed salt as a pottery colour. A. G. Bergman prepared **uranyl cobaltous phosphate**,  $\text{Co}(\text{UO}_2)_2(\text{PO}_4)_2$ .

According to H. Debray,<sup>2</sup> **cobaltous hydrophosphate**,  $\text{CoHPO}_4 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ , is formed by digesting cobaltous carbonate with phosphoric acid, and boiling the acidic soln.; and the same *hemitriphosphate*,  $\text{CoHPO}_4 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ , also by boiling a soln. of cobaltous dihydrophosphate with a cobaltous salt. F. Ephraim and C. Rossetti observed that the hydrated hydrophosphate,  $\text{CoHPO}_4 \cdot n\text{H}_2\text{O}$ , is a well-defined, crystalline compound. C. H. D. Bödeker prepared the *hemipentahydrate*,  $\text{CoHPO}_4 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ , in pale violet-red crystals, by adding an excess of sodium hydrophosphate to a soln. of cobaltous chloride, dissolving half the lilac-red precipitate in the smallest possible quantity of hydrochloric acid, digesting the other half with the soln. so obtained, and allowing the liquid to stand for some time. H. Bassett and W. L. Bedwell studied the constitution of the salt. R. F. Weinland and co-workers obtained a complex salt with pyridine, viz.,  $2\text{CoHPO}_4 \cdot 7\text{C}_5\text{H}_5\text{N} \cdot 8\text{H}_2\text{O}$ , as a rose-red, crystalline powder.

H. Debray prepared **sodium cobaltous hydrophosphate**,  $\text{Co}_3(\text{PO}_4)_2 \cdot 2\text{Na}_2\text{HPO}_4 \cdot 8\text{H}_2\text{O}$ , by adding an excess of sodium hydrophosphate to a soln. of a cobaltous salt, digesting the gelatinous precipitate with an excess of a soln. of sodium hydrophosphate at  $80^\circ$  for 15 to 20 days; the blue liquid which is formed deposits the salt in blue, tabular crystals. This salt was also prepared by H. Bassett and W. L. Bedwell.

A. Reynoso<sup>3</sup> heated cobaltous pyrophosphate with water, in a sealed tube, at  $280^\circ$  for 5 to 6 hrs.; cobaltous orthophosphate is precipitated in rose-red, octahedral crystals, and **cobaltous dihydrophosphate**,  $\text{Co}(\text{H}_2\text{PO}_4)_2$ , remains in soln. The evaporation of the soln. yields a gum-like mass of the dihydrophosphate. The aq. soln. is decomposed by alcohol.

H. Debray observed that when precipitated ammonium cobaltous phosphate is digested with a conc. acidic soln. of ammonium phosphate for 7 or 8 days, it forms rose-red, insoluble crystals of **ammonium cobaltous dihydrophosphate**,  $(\text{NH}_4)\text{CoPO}_4 \cdot (\text{NH}_4)_2\text{H}_2\text{PO}_4 \cdot 4\text{H}_2\text{O}$ .

According to F. Schwarz,<sup>4</sup> if a soln. of a cobaltous phosphate be treated with sodium triphosphate, **cobaltous triphosphate**,  $\text{Co}_m\text{H}_{5-2m}\text{P}_3\text{O}_{10} \cdot n\text{H}_2\text{O}$ , is formed as an amorphous precipitate contaminated with a sodium salt. The precipitate quickly re-dissolves. It was also prepared by M. Stange, and P. Glühmann. F. Schwarz mixed a soln. of a gram of octahedral sodium triphosphate, in the least possible quantity of water, with 1.5 to 1.75 grms. of cobalt sulphate. The rose-red precipitate, unwashed, was dried on a porous tile. The analyses of the **sodium cobaltous triphosphate** approximate  $\text{NaCo}_2\text{P}_3\text{O}_{10}$ , but they varied so much that it might be questioned if a chemical individual is formed under these conditions. A *dodecahydrate* was obtained from soln. of sodium triphosphate and a cobaltous salt in dil. aq. soln. The rose-red crystals become blue when dehydrated, and they fuse to a blue glass; they are easily soluble in acids; and, according to M. Stange, they are isomorphous with those of the corresponding nickel salt.

According to F. Stromeyer,<sup>5</sup> H. Rose, A. Terreil, and A. Roseheim and co-workers, the precipitate which a soln. of a cobaltous salt furnishes when treated with sodium pyrophosphate, is **cobaltous pyrophosphate**,  $\text{Co}_2\text{P}_2\text{O}_7$ ; it is soluble in an excess of the precipitant, forming a deep green soln. from which it is precipitated when it is allowed to stand for some time. H. D. Dakin obtained it by igniting ammonium cobaltous phosphate. The salt was studied by H. Bassett and W. L. Bedwell. F. W. Clarke found the sp. gr. to be 3.746 at  $23^\circ$ , and 3.710 at  $25^\circ$ . E. F. Herroun, and P. Pascal studied the magnetic properties. A. Reynoso found that when the pyrophosphate is heated, in a sealed tube, with water for some hours at  $280^\circ$  to  $300^\circ$ , it is resolved into acid and normal phosphate. A. Schwarzenberg said that it is insoluble in aq. ammonia. J. A. Hedvall and



H. Heuberger studied the reactions with alkaline earth oxides whereby orthophosphates are formed.

According to C. D. Braun, if cobaltic hexamminometaphosphate be calcined, a smalt-blue powder is formed having the composition  $6\text{CoO} \cdot 5\text{P}_2\text{O}_5$ ; and if cobaltic hexamminohydrophosphate be calcined, the violet powder has the composition  $3\text{CoO} \cdot 2\text{P}_2\text{O}_5$ .

L. Ouvrard prepared **sodium cobaltous pyrophosphate**,  $4\text{Na}_2\text{P}_2\text{O}_7 \cdot 5\text{Co}_2\text{P}_2\text{O}_7$ , by fusing a mixture of sodium metaphosphate and cobalt oxide; and K. A. Wallroth, by melting microcosmic salt with cobalt oxide,  $\text{Co}_3\text{O}_4$ . The salt furnishes dichroic, violet-red prisms isomorphous with the corresponding nickel salt. The sp. gr. is 3.2 at  $20^\circ$ . P. Pascal noted the formation of complexes when freshly-precipitated cobalt pyrophosphate is dissolved in an excess of a soln. of sodium pyrophosphate; and the sp. magnetic susceptibility of the soln. is  $3.03 \times 10^{-7}$  mass unit.

J. H. Gladstone observed that when a feebly ammoniacal soln. of cobalt nitrate is treated with pyrophosphotriaminic acid, violet **cobalt triamidopyrophosphate** is formed.

R. Maddrell<sup>6</sup> evaporated to dryness a soln. of cobalt sulphate in an excess of phosphoric acid, and heated the residue to  $316^\circ$ . A rose-red powder of **cobaltous monometaphosphate**,  $\text{Co}(\text{PO}_3)_2$ , is formed, insoluble in water and dil. acids, but soluble in conc. sulphuric acid. A. Glatzel said that the metaphosphate is perceptibly soluble in boiling hydrochloric or nitric acid; it melts at a red-heat, and on cooling it forms a glassy mass. When heated with alkali sulphide soln., cobalt sulphide is precipitated, and alkali metaphosphate remains in soln.

A. Glatzel obtained **cobaltous dimetaphosphate**,  $\text{Co}_2(\text{PO}_3)_4$ , as a rose-red precipitate on treating a soln. of cobalt chloride with sodium metaphosphate. When heated, the hydrate becomes blue; gives off its water of hydration at a dull red-heat; and then melts, forming, when cold, a glassy mass. P. Hautefeuille and J. Margottet obtained a metaphosphate by melting cobalt oxide with metaphosphoric acid. C. D. Braun obtained the dimetaphosphate by calcining crystals of cobaltic aquopentamminopyrophosphate. The smalt-blue product forms a brown soln. and brown powder when treated with conc., aq. ammonia; potash-lye forms a rose-red powder, and when heated, a blue soln. which gradually oxidizes and deposits hydrated cobaltic oxide. A. Glatzel said that 1 part of the dimetaphosphate dissolves in 25 parts of water; and it dissolves in boiling mineral acids—particularly sulphuric acid. Cold, conc. sulphuric acid does not dissolve the salt, but the hot acid does so, leaving behind a carmine-red powder which is soluble in water. G. Tammann found that if an excess of a cobalt salt is added to a soln. of sodium dimetaphosphate, **sodium cobaltous dimetaphosphate** is formed.

G. Tammann obtained **cobaltous trimetaphosphate**,  $\text{Co}_3(\text{PO}_3)_6 \cdot 9\text{H}_2\text{O}$ , by treating sodium trimetaphosphate with cobalt chloride or sulphate. The product is sparingly soluble in water. G. Tammann, and G. Tammann and A. Hollander obtained **disodium tricobaltous trimetaphosphate**,  $\text{Na}_2\text{P}_2\text{O}_6 \cdot \text{Co}_3(\text{PO}_3)_6$ , as a purple powder consisting of cubic and octahedral crystals, by fusing cobalt sulphate and sodium ammonium hydrophosphate. The salt is insoluble in conc. acids. G. Tammann also treated a soln. of a cobalt salt with one of sodium dimetaphosphate, in equivalent proportions, 3:1, and obtained a precipitate approximating the *henicosihydrate*,  $\text{Na}_2\text{P}_2\text{O}_6 \cdot \text{Co}_3(\text{PO}_3)_6 \cdot 21\text{H}_2\text{O}$ . R. Maddrell obtained **sodium tricobaltous trimetaphosphate**,  $\text{NaPO}_3 \cdot \text{Co}_3(\text{PO}_3)_6$ , by evaporating a soln. of phosphoric acid, sodium phosphate, and cobalt sulphate to a syrup, and then heating the product to  $316^\circ$ . The rose-red salt is insoluble in water and dil. acids, but soluble in conc. sulphuric acid. L. Ouvrard reported **tetrasodium cobaltous trimetaphosphate**,  $\text{Na}_4\text{Co}(\text{PO}_3)_6$ , to be formed by melting a mixture of sodium pyrophosphate and a little cobalt oxide, or sodium orthophosphate and cobalt oxide. The crystals have a sp. gr. 2.5 at  $20^\circ$ , and are isomorphous with those of the corresponding

zinc salt. C. G. Lindbom, and T. Fleitmann and W. Henneberg reported an *octohydrate*,  $\text{Na}_4\text{Co}(\text{PO}_3)_6 \cdot 8\text{H}_2\text{O}$ , soluble in water. A. Mente prepared **cobalt nitrilotrimetaphosphate**,  $\text{CoNP}_3\text{O}_7 \cdot \text{H}_2\text{O}$ , by treating a dil. soln. of the acid with cobalt nitrate. The red salt is insoluble in water, slightly soluble in dil. acids, and easily soluble in aq. ammonia. It is decomposed by sodium hydroxide or carbonate, and by ammonium sulphide.

H. Rose observed that sodium hexametaphosphate gives a red precipitate of **cobaltous hexametaphosphate**,  $\text{Co}_6(\text{PO}_3)_{12} \cdot n\text{H}_2\text{O}$ , when added to a soln. of cobalt chloride, but not the sulphate.

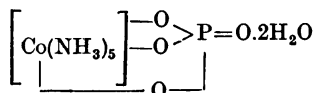
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## § 30. Cobaltic Phosphates

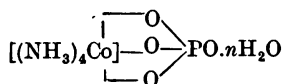
G. D. Braun<sup>1</sup> obtained **cobaltic hexamminorthophosphate**,  $[\text{Co}(\text{NH}_3)_6]\text{PO}_4 \cdot 4\text{H}_2\text{O}$ , by mixing soln. of the hexamminochloride with sodium orthophosphate. The salt was also obtained by O. W. Gibbs, M. Porumbaru, and G. Vortmann. S. M. Jörgensen mixed a warm soln. of 2 grms. of the corresponding nitrate in 200 c.c. of water and 10 to 20 c.c. aq. ammonia, with 3 grms. of normal sodium phosphate in 100 c.c. of water, and washed the precipitate with cold water. The golden-yellow, acicular crystals of the *tetrahydrate*, dried in air, lose their water of hydration at  $100^\circ$  to  $130^\circ$ . W. Biltz observed that when the salt is heated for 3 days at  $190^\circ$  to  $200^\circ$  in a current of carbon dioxide, it furnishes cobaltous pyrophosphate, and the gaseous products—ammonia, water, and nitrogen. E. Birk and W. Biltz gave 1.864 for the sp. gr. of the crystals at  $25^\circ/4^\circ$ ; and 137.4 for the mol. vol. P. Mosimann, and F. Ephraim and co-workers observed that a sat., aq. soln. at  $18^\circ$  contains 0.033 grm. or 0.00055 mol of the salt per litre.

R. Klement prepared **cobaltic aquopentamminorthophosphate**,  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{PO}_4 \cdot 2\text{H}_2\text{O}$ , by the action of normal sodium phosphate on the corresponding nitrate, and he also prepared it from the mother-liquor left in making the phosphatotetrammines. The brownish-red crystals are sparingly soluble in water, and the mol. conductivities of soln. with a mol of the salt in 1000 and 2000 litres of water, are, respectively, 214, and 253. The aq. soln. has an alkaline reaction, and gives an immediate precipitation of silver phosphate when it is treated with silver nitrate; conc. hydrochloric acid converts the salt slowly into the aquopentamminochloride. The basic salt reported by S. M. Jörgensen is considered to be a hydroxypentamminophosphate. J. C. Duff reported **cobaltic orthophosphatopentamminophosphate**, which he represented by the formula :

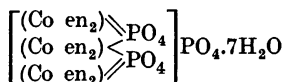


It is usually formulated as a **cobaltic phosphatopentammine**,  $[\text{Co}(\text{NH}_3)_5(\text{PO}_4)] \cdot 2\text{H}_2\text{O}$ , in which the pentammine, being associated with a trivalent acid radicle in the nucleus, is nullvalent. A pentammine with a dibasic acid radicle in the complex is univalent; and with a monobasic acid radicle in the complex, bivalent. R. Duval prepared a similar compound. J. C. Duff obtained the phosphatopentammine in brick-red, flattened needles by using as precipitant for aquopentamminonitrate a soln. of 6.73 grms. of hydrated sodium hydrophosphate to which 18.75 c.c. of *N*-NaOH had been added to make the normal phosphate. The salt does not lose water at  $100^\circ$ ; it is sparingly soluble in warm water; and gives a precipitate with silver nitrate, but not with ferric chloride. The measurements of the mol. conductivity places the salt in the same class as the carbonato- and similar pentamminosalts, but not with the aquopentammines. The compound was also prepared by C. Duval; but R. Klement could not satisfy himself that the salt is a phosphatopentammine.

R. Klement obtained **cobaltic diaquotetramminorthophosphate**,  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{PO}_4$ , by mixing warm, equivalent soln. of the diaquo-chloride and normal sodium phosphate. The brick-red crystalline powder is sparingly soluble in water, and the aq. soln. has an alkaline reaction, and it gives a precipitate with silver nitrate. If dichlorodiaquodiamminochloride or dichloro-aquotriamminochloride be warmed with an aq. soln. of sodium hydrophosphate, a green powder is formed consisting of cobaltous phosphate and **cobaltic phosphatotetrammine**,  $[\text{Co}(\text{NH}_3)_4(\text{PO}_4)] \cdot n\text{H}_2\text{O}$ , or :



where  $n$  may be 2 or 3. The tetrammine is separated by boiling the green powder with a soln. of ammonium phosphate and conc., aq. ammonia, and allowing the violet liquid to cool. The salt can be purified by dissolution in very dil. hydrochloric acid, and precipitation with dil. ammonia. The violet plates very readily lose their water of hydration. The electrical conductivities of soln. with a mol of the salt in 1000 and 2000 litres of water are, respectively, 37 and 65. The salt is sparingly soluble in water; the aq. soln.—0.001 mol per litre—gives no precipitate with silver nitrate; conc. hydrochloric acid forms a mixture of cis- and trans-dichloro-chloride; oxalic acid yields the cis-diaquo-oxalate; and liquid ammonia does not react with the salt. R. Vogel reported **cobaltic chlorobisethylenediaminepyridinephosphate**, and also **cobaltic diphosphatobisethylenediaminephosphate**,



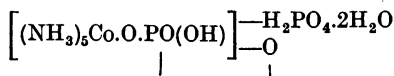
A similar salt, **cobaltic diphosphatobispropylenediaminephosphate**,  $[(\text{Co en}_2)_3(\text{PO}_4)_2]\text{PO}_4 \cdot 14\text{H}_2\text{O}$ , was prepared by A. Werner and A. Frölich by the action of a soln. of sodium phosphate on the corresponding dichloro-chloride.

C. D. Braun<sup>2</sup> prepared **cobaltic hexamminohydrophosphate**,  $[\text{Co}(\text{NH}_3)_6]_2(\text{HPO}_4)_3 \cdot 4\text{H}_2\text{O}$ , by adding a soln. of sodium hydrophosphate to a soln. of a soluble hexammino-salt. The product was probably impure, because his formula very nearly corresponds with  $3[\text{Co}(\text{NH}_3)_6]\text{PO}_4 \cdot \text{H}_3\text{PO}_4 \cdot 5\frac{1}{2}\text{H}_2\text{O}$ , whereas that prepared by S. M. Jörgensen agrees with that of the tetrahydrate just indicated. S. M. Jörgensen obtained the salt by mixing a soln. of 3 grms. of the hexamminochloride in water acidified with acetic acid with an aq. soln. of 6 grms. of sodium hydrophosphate; and also by neutralizing an aq. soln. of the hexamminocarbonate with 10 per cent. phosphoric acid. The brownish-yellow crystals of the *tetrahydrate* are stable over sulphuric acid, but 3 mols. of water are lost in about a couple of hours at 100°, and the remaining water is given off more slowly. The hydrophosphate is soluble in dil. hydrochloric acid; nitric acid converts it into the hexamminonitrate; and an excess of aq. ammonia converts it into the normal phosphate.

C. and M. Duval prepared **cobaltic phosphatopentamminochloride**,  $[\text{Co}(\text{PO}_4)(\text{NH}_3)_5]\text{Cl}$ . S. M. Jörgensen reported **cobaltic aquopentamminohydrophosphate**,  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]_2(\text{HPO}_4)_3 \cdot 4\text{H}_2\text{O}$ , to be formed by mixing a soln. of the corresponding carbonate with the theoretical proportion of 10 per cent. phosphoric acid. Oily drops separate from the filtrate, and crystals are formed; then the liquid is allowed to stand in a cool place for a few days. The crystals resemble those the corresponding hexammine. The *tetrahydrate* loses no water over sulphuric acid, but at 100°, it rapidly loses 5 mols. of water, and more is lost slowly at this temp. The salt is sparingly soluble in cold water, and readily soluble in hot water. The undissolved salt melts under hot water, to form a viscid, reddish-brown mass which becomes pale red on cooling.

A. Werner and E. Kindscher prepared **cobaltic diol-octamminohydrophosphate**,  $[(\text{NH}_3)_4\text{Co} \cdots (\text{OH})_2 \cdots \text{Co}(\text{NH}_3)_4](\text{HPO}_4)_2 \cdot 6\text{H}_2\text{O}$ , by the action of sodium hydrophosphate on the corresponding chloride. The rose-red crystals of the *hexahydrate* are insoluble in water.

J. C. Duff<sup>3</sup> reported a **cobaltic phosphatopentamminodihydrophosphate**, which he represented by the formula:  $[\text{Co}(\text{NH}_3)_5(\text{HPO}_4)]\text{H}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ , or rather:



to be formed by adding 5 grms. of the carbonato-nitrate to a soln. of 3 grms. of orthophosphoric acid in 25 c.c. of water at 40°. The salt is said to be very sparingly soluble in cold water, readily soluble in dil. alkali-lye, or dil. mineral

acids. The water of crystallization is lost by the *dihydrate* over sulphuric acid. The salt melts in the steam-oven. R. Duval prepared the complex:  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{PO}_4)](\text{H}_2\text{PO}_4)_2 \cdot 4\text{NH}_4\text{NO}_3$ . L. Dede studied the subject.

C. D. Braun,<sup>4</sup> O. W. Gibbs, G. Vortmann, and M. Porumbaru studied the preparation of **cobaltic hexamminopyrophosphate**,  $[\text{Co}(\text{NH}_3)_6]_4(\text{P}_2\text{O}_7)_3 \cdot 20\text{H}_2\text{O}$ . S. M. Jörgensen said that when a cold soln. of the hexamminochloride is treated with a soln. of sodium pyrophosphate, the precipitate approximates  $[\text{Co}(\text{NH}_3)_6]\text{NaP}_2\text{O}_7 \cdot 11\frac{1}{2}\text{H}_2\text{O}$ , and when this is washed with hot water, it is converted into the normal *icosihydrate*. If hot soln. of the component salts are mixed, say at 80° to 85°, **sodium cobaltic hexamminopyrophosphate**,  $[\text{Co}(\text{NH}_3)_6]_6(\text{P}_2\text{O}_7)_3(\text{NaP}_2\text{O}_7) \cdot 39\text{H}_2\text{O}$ , is formed in yellowish-brown crystals which lose most of their water of hydration when confined over sulphuric acid. The other sodium cobaltic hexamminopyrophosphate retains its composition when washed with cold water, and it furnishes brownish-yellow, six-sided plates, sparingly soluble in water. The salt loses 8 mols. of water over sulphuric acid; and 11 mols. at 100°. This salt was discussed by A. Rosenheim and T. Triantaphyllides. W. Lenz observed no fluorescence with ultra-violet rays.

Returning to the normal icosihydrated hexamminopyrophosphate, S. M. Jörgensen prepared it by treating a cold soln. of the hexamminonitrate with potassium pyrophosphate; or as indicated above. The brownish-yellow, six-sided crystals lose 15 mols. of water very slowly over sulphuric acid, and the salt decomposes at 100°. The salt is almost insoluble in hot and cold water. S. M. Jörgensen said that an acid pyrophosphate, **cobaltic hexamminohydropyrophosphate**,  $[\text{Co}(\text{NH}_3)_6]\text{HP}_2\text{O}_7$ , is produced when the precipitation is made in soln. acidified with acetic acid. The dark orange-yellow, prismatic crystals are almost insoluble in water, and they are stable in boiling water; soluble in dil. hydrochloric acid; and are converted by dil. soda-lye into the sodium cobaltic salt. The acid salt was discussed by A. Rosenheim and T. Triantaphyllides. W. Lenz observed no fluorescence in ultra-violet light.

M. Porumbaru reported that when the double salt with sodium precipitated on adding an excess of sodium pyrophosphate to a soln. of chloropentamminochloride, is washed with luke-warm water, **cobaltic aquopentamminopyrophosphate**,  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]_4(\text{P}_2\text{O}_7)_3 \cdot 12\text{H}_2\text{O}$ , is formed. S. M. Jörgensen obtained it by adding the theoretical proportion of sodium pyrophosphate to a soln. of the corresponding sulphate. The red, hexagonal, acicular crystals of the *dodecahydrate* lose 6 mols. of water over sulphuric acid, and 13 mols. of water are lost at 100°. If a soln. of 5 grms. of the aquo-nitrate in 45 c.c. of water and 10 c.c. of 45 per cent. acetic acid, at 80°, is mixed with a soln. of 2 mols. of sodium pyrophosphate in 80 c.c. of water, also at 80°, rectangular prisms of **cobaltic aquopentamminohydropyrophosphate**,  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{HP}_2\text{O}_7$ , are formed. The salt is insoluble in water, soluble in dil. acetic acid, and freely soluble in dil. hydrochloric acid. If the salt be shaken with dil. soda-lye, it forms **sodium cobaltic aquopentamminopyrophosphate**,  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{NaP}_2\text{O}_7 \cdot 11\frac{1}{2}\text{H}_2\text{O}$ . This salt was also described by C. D. Braun, O. W. Gibbs, and, as indicated above, by M. Porumbaru. S. M. Jörgensen obtained it by adding an excess of sodium pyrophosphate to an aq. soln. of the aquo-sulphate. The salt yields hexagonal prisms when re-crystallized from dil. aq. ammonia.

S. M. Jörgensen prepared **cobaltic diaquotetramminopyrophosphate**,  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]_4(\text{P}_2\text{O}_7)_3 \cdot 6\text{H}_2\text{O}$ , by adding a 4 per cent. aq. soln. of sodium pyrophosphate to a conc. soln. of the diaquo-sulphate in eq. proportions, and washing the precipitate with water. The *hexahydrate* slowly loses 4 mols. of water over sulphuric acid, and 6 mols. at 100°. The salt is insoluble in water, but easily soluble in dil. acids. If the cold soln. in conc. sulphuric acid is treated with hydrochloric acid, the diaquo-chloride is formed.

C. D. Braun, and O. W. Gibbs obtained **cobaltic chloropentamminopyrophosphate**,  $[\text{Co}(\text{NH}_3)_5\text{Cl}]_2\text{P}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$ , by the action of a soln. of sodium pyrophosphate

on a soln. of the chloro-chloride. S. M. Jörgensen recommended shaking soln. of eq. proportions of the chloro-nitrate and sodium pyrophosphate, and shaking the filtrate with alcohol. The violet-red needles lose 3 or 4 mols. of water at 100°. The salt is easily soluble in water, and the soln. has an alkaline reaction. If a very conc., cold, aq. soln. of the chloro-nitrate be treated with a mixture of sodium dihydropyrophosphate with a little free pyrophosphoric acid, or with pyrophosphoric acid alone, and then with alcohol, violet-red needles of **cobaltic chloropentamminohydropyrophosphate**,  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{H}_2\text{P}_2\text{O}_7$ , are formed. The salt is sparingly soluble in cold water, easily soluble in hot water; and with dil. hydrochloric acid, it forms the chloro-chloride, and with hydrofluosilicic acid, the chloro-fluosilicate.

C. and M. Duval prepared **sodium cobaltic pyrophosphatopentamminocobaltate**,  $\text{Na}[\text{Co}(\text{P}_2\text{O}_7)(\text{NH}_3)_5]$ .

C. D. Braun<sup>5</sup> obtained a **cobaltic hexamminochlorometaphosphate**, which F. M. Jäger represented by the assumed formula:  $[\text{Co}(\text{NH}_3)_6]\text{Cl}(\text{PO}_3)_2 \cdot n\text{H}_2\text{O}$ . It was obtained by evaporating the mother-liquid obtained in the preparation of the hydrophosphate. The reddish-yellow scales were found by F. M. Jäger to be rhombic bipyramids with the axial ratios  $a : b : c = 0.9866 : 1 : 1.044$ .

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